THE SYNTHESIS OF ANTIMONY-NITROGEN COMPOUNDS BY AMMONOLYSIS AND CHLORAMINATION REACTIONS

By

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CHAPTER I

INTRODUCTION

Aqueous chloramine was first prepared by Raschig in 1907 (1) by mixing dilute solutions of ammonia and hypochlorite ion.

$$NH_3 + OCl^- \rightarrow NH_2Cl + OH^-$$

Mattair and Bisloe (2) succeeded in preparing anhydrous gaseous chloramine in 1951 by the gas phase reaction of excess ammonia with chlorine.

$$2NH_{3(g)} + Cl_{2(g)} \rightarrow N_2H_{(g)} + NH_4Cl_{(s)}$$

The chloramine reaction with Lewis bases has been the subject of a rather extensive investigation in this laboratory for a number of years. It was found that chloramine reacts with trialkylamines to form the corresponding 1,1,1-trialkylhydrazinium chloride (3),

$$R_3N + NH_2Cl \rightarrow [R_3\overset{+}{N}NH_2]Cl^-$$

Chloramine failed to react with triphenylamine. Dialkyl- and trialkylphosphines also react with chloramine to produce aminophosphonium chlorides (4),

$$R_3P + NH_2Cl \rightarrow [R_3\overset{+}{P}NH_2]Cl^-$$

Very recent work (5) in this laboratory has shown that the

chloramination of trialkyl- and triarylarsines gives good yields of aminoarsonium chlorides.

$$R_3As + NH_2Cl \rightarrow [R_3AsNH_2]Cl$$

However, rigorously anhydrous conditions must be maintained to prevent hydrolysis of the products obtained.

Other work using solutions of ammonia-free chloramine (6) has been reported. The ammonia-chloramine mixture from the gas phase reaction was passed into a solvent, usually ether, and then freed of ammonia and all traces of water by slowly passing the solution through a column of anhydrous copper sulfate. Vacuum-line technique was then used to maintain rigorously anhydrous conditions throughout the remainder of each experiment.

Since compounds of the first three members of group V of the periodic table were being rather extensively studied with respect to their reaction with chloramine, the next logical step was a similar investigation of antimony compounds. This, therefore, has been one of the major purposes of this work.

In 1964, Wittig and Hellwinkel (7) carried out the reaction of triphenylstibine with Chloramine-T and obtained $(C_6H_5)_3Sb{=}N{-}SO_2C_6H_4CH_3$, which is probably the first compound isolated containing a direct Sb(V)-N linkage. Some early (8) and also some more recent work (9) involving the hydrolysis of various trialkyldihalostibanes gave evidence

for the formation of compounds of the type $R_3Sb(OH)Cl$. Appel and co-workers (10) describe the formation of $[(C_6H_5)_3SbNH_2]X$ (X = Cl, Br, and I) from the reaction of triphenylstibine imine with a variety of reagents. However, other workers (11,12,13,14) have shown that partial hydrolysis of trialkyl- and triaryldichlorostibanes yields the anhydride-like compounds $[R_3Sb(Cl)]_2O$, and not the hydroxy chlorides. On the basis of all the above information, it was postulated that chloramine would react with various tertiary stibines to yield compounds of the type $[R_3Sb(Cl)]_2NH$, possibly going through the intermediate $R_3Sb(NH_2)Cl$.

Another major purpose of this work has been to study the reactions of liquid ammonia and liquid ammonia-potassium amide with triphenyldichlorostibane and tetraphenylbromostibane in order to obtain some new and interesting antimony-nitrogen compounds. Since the onset of this work, Appel et al. (10), reported the findings of a very extensive study of the reaction of $(C_6H_5)_3SbX_2$ (X = Cl, Br, and I) with some alkali metal amides in liquid ammonia. The reaction conditions were such that both halogen atoms were removed from the antimony, producing triphenylstibine imine and in one case the condensation product of the imine, $(C_6H_5)_3Sb{=}N{-}Sb(C_6H_5)_3{-}N{=}Sb(C_6H_5)_3$.

Finally, an objective of this work has been to carry out a qualitative infrared and proton magnetic resonance study on as many organoantimony compounds as possible in order to: (1) make tentative assignments to new absorption bands in the infrared spectra; (2) learn more about the polarity of the antimony-halogen bonds; (3) make specific nuclear magnetic resonance data available.

CHAPTER II

THE SYNTHESIS OF ANTIMONY-NITROGEN COMPOUNDS BY CHLORAMINATION WITH AMMONIA-FREE CHLORAMINE, AND SUBSEQUENT REACTIONS OF THE PRODUCTS

Experimental

Materials

Tri-*n*-butyl- and triphenylstibine were purchased from M and T Chemicals, Inc. The former was redistilled and the fraction boiling at 129-130°C. (11 mm) was used. Triphenylstibine was recrystallized from petroleum ether before use. The solid melted at 52-54°C. Reagent grade solvents were dried over calcium hydride. Technical grade solvents were distilled from calcium hydride, then stored over it.

Analyses

Elementary analyses were performed by Schwarzkopf Microanalytical Laboratory, Woodside, New York, Crobaugh Laboratories, Charleston, West Virginia and Galbraith Laboratories, Inc., Knoxville, Tennessee. Chloride analyses were usually carried out in this laboratory by the Volhard technique. Melting points were obtained using wax sealed capillaries on a Thomas-Hoover capillary melting point apparatus and are uncorrected.

Molecular weights were determined by the cryoscopic method using benzene as a solvent. A conventional freezing point apparatus was modified to provide a slight flow of dry nitrogen in order to minimize solution contact with the atmosphere. The lower than theory molecular weights reported for the nitrogen-containing compounds are indicative of partial hydrolysis which undoubtedly occurred during the determination.

Infrared spectra

Infrared spectra were obtained on a Beckman Model IR 10 infrared spectrophotometer using potassium bromide and cesium iodide optics. Solid state spectra were obtained using Nujol and Kel-F mulls. The spectra of all the trialkylstibines were obtained using thin films. All water and oxygen sensitive samples were prepared in a dry box and were stored in a dessicator until being placed on the instrument, which was constantly being purged with a slow stream of nitrogen. The infrared spectral absorptions are listed in Table 1.

Proton magnetic resonance spectra

The proton magnetic resonance spectra were obtained with either a Varian high resolution nuclear magnetic resonance spectrometer, Model V-4300-2, provided with field homogeneity control, magnet insulator, and field stabilizer, operating at 56.4 or 60 Mc or with a Varian nuclear magnetic

TABLE 1

INFRARED SPECTRAL DATA, Cm^{-1} [a]

$(CH_3)_3Sb$ Neat	2990(m),2915(m),1390(w),810(m), 512(s)
$(CH_3)_3SbBr_2$ [13] Nujol	3012(w),2927(w),2410(vw),1772(vw), 1723(vw),1403(vw),1387(w),1332(vw), 1210(vw),870(s),564(m)
$(CH_3)_3SbCl_2$ Nujol	1210(w),870(vsb),578(s),277(s)
$(CH_3)_3Sb(ONO_2)_2$ Kel-F, Nujol	3035(w),2938(vw),2798(vw),2240(vw), 1915(vw),1805(vw,b),1755(vw), 1665(v,b),1550-1500(vs),1400(m), 1300-1270(s),1240(m),1228(m), 965(vs),862(vs),833(m),792(m), 728(s),708(m),578(m),305(w,sh), 278(m)
$[(CH_3)_3Sb(Cl)]_2NH$ Nujol	3225(m),2420(vw),2330(vw),2055(vw), 1800(vw),1750(vw),1645(vw,b), 1408(m),1238(vw,sh),1209(w),1098(vw), 1055(vw),861(vs),741(vs),580(s), 533(w)
$[(CH_3)_3Sb(Cl)]_2O$ KBr Pellet, Nujol	3010(vw),2920(vw),2420(vw),1800(vw), 1749(vw),1405(m),1228(w),1217(vw), 860(s),771(s,b),585(s),534(m), 285(w,b),265(w)
$[(CH_3)_3Sb(ONO_2)]_2O$ Kel-F, Nujol	3010(m),2730(vw),2440(vw,d),2010(vw,d), 1795(w,b),1720(w,b),1480-1330(vs), 1310-1275(vs),1238(w),1222(w), 1018(vs),860(s),815(vs,sh),788(vs,b), 715(vs),578(s),530(m),260(vw)
$(C_2H_5)_3Sb$ Neat	2960(vs),2920(vs),2880(s),2835(w), 2740(vw),1465(m),1428(w),1380(m), 1235(vw),1185(m),1025(m),965(w,b), 700(m),685(m,sh),655(w,sh),500(m)

Table 1 (cont'd)

$[(C_2H_5)_3Sb(Cl)]_2NH$ Nujol	3162(m,b),1670(vw,b),1284(vw), 1212(m,sh),1193(s),1026(s),972(s), 758(vs),704(vs),538(m,sh),528(m), 497(w)
$[(C_2H_5)_3Sb(Cl)]_2O$ Nujol	2760(vw),2166(vw),1404(m),1200(s), 1063(w,sh),1025(m),971(m),768(s,b), 713(s,b),647(m,sh),545(m),498(vw), 300(w,b),265(w)
$[(C_2H_5)_3Sb(ONO_2)]_2O$ Nujol	2285(vw),1715(vw),1480-1420(vs), 1285(vs),1220(w,sh),1208(m),1095(w), 1025(s,sh),1013(vs),980(m),815(s,sh), 792(vs),702(vs),546(m),498(m)
$(n\text{-}C_3H_7)_3Sb$ Neat	2960(vs),2936(vs),2905(s),2870(s), 2820(w,sh),1460(m,sh),1455(m), 1415(vw),1373(w),1332(w),1275(w), 1190(vw),1170(w,sh),1155(w),1068(w), 1020(vw),995(vw),800(vw),720(vw,b), 680(vw,b),655(w,sh),585(w),500(w)
$[(n\text{-}C_3H_7)_3Sb(Cl)]_2NH$ Nujol	3142(m),1657(vw,b),1417(w),1337(vw), 1242(vw),1202(w),1174(m),1164(w,sh), 1076(s),1012(s),815(w),752(vs), 692(s),665(vw,sh),613(w),595(vw), 516(vw),422(w)
$[(n\text{-}C_3H_7)_3Sb(Cl)]_2O$ KBr Pellet, Nujol	2960(m),2930(m),2870(m),1455(m), 1413(w),1373(w),1335(w),1278(w), 1167(s),1075(s),1017(vw,sh),1008(s), 802(vw,sh),754-734(s,d),696(s), 628(w),607(w),522(w),395(w),300(m), 285(m,sh),260(m)
$(n\text{-}C_4H_9)_3Sb$ Neat	2960(vs),2930(vs),2880(s),2860(s), 2753(vw),1460(s),1420(w),1378(m), 1360(vw),1351(w),1294(w),1250(w), 1178(w),1148(w),1080(w),1050(vw), 1022(vw),1005(w),961(w),876(w,b), 770(vw),745(vw),686(w,b),590(w), 500(w)
$(n\text{-}C_4H_9)_2SbCl$ Neat	2965(vs),2930(vs),2880(s),2870(s), 2740(vw),1463(s),1412(w),1380(m), 1360(vw),1344(w),1295(w),1250(w), 1180(w),1152(w),1082(w),1050(vw), 1025(vw),1005(vw),965(w),868(w,b), 850(vw,sh),772(vw),748(vw),678(w,b), 590(w),505(w)

Table 1 (cont'd)

$(\underline{n}\text{-}C_4H_9)_3SbCl_2$ Neat	2970(vs),2940(vs),2880(s),2740(vw), 1468(s),1410(m),1388(m),1350(w), 1295(w),1255(m),1170(m),1095(m), 1048(w),1005(vw),960(vw),890(m), 860(w),780(w),712(m),615(vw),512(vw)
$[(\underline{n}\text{-}C_4H_9)_3Sb(Cl)]_2NH$ Nujol	3162(m),2181(w),1582(w,b),1395(s), 1252(w,b),1164(s),1082(s),1030(m), 1002(w,sh),962(vw),883(m),768(vs), 736(vs),698(vs),615(vw),511(vw)
$[(\underline{n}\text{-}C_4H_9)_3Sb(Cl)]_2O$ Carbon disulfide, Nujol	2965(vs),2930(vs),2870(s),1572(vw,b), 1405(m),1343(m),1294(m),1253(vw), 1181(s),1165(s),1081(m),1028(m), 994(w,sh),885(s),855(m,sh),770(vs), 743(vs),693(vs),620(w),562(w),524(w), 460(vw,b),400(w),260(w)
$(C_6H_5)_3Sb$ Nujol	3060(w),3040(w),1960(vw,b),1880(vw,b), 1820(vw,b),1572(w),1475(m),1428(s), 1328(vw),1295(w),1178(m),1150(w), 1060(m),1012(w),992(w),900(vw), 850(vw),721(vs),689(vs),450(m)
$(C_6H_5)_3SbCl_2$ Nujol	3050(vw),1572(w),1475(s),1430(vs), 1326(w),1300(w),1172(w),1155(w), 1053(vw),1012(w),990(m),740(m), 725(vs),678(s),450(m),277(m)
$[(C_6H_5)_3Sb(Cl)]_2NH$ Nujol	3140(w),3070(vw,sh),3040(m),1570(m), 1475(s),1430(vs),1329(m),1302(m), 1268(vw),1180(m),1157(m),1090(vw), 1061(s),1019(s),995(vs),985(w), 975(w),969(w),915(m),880(vw,sh), 850(w),840(vw,sh),765(vs),735(vs), 690(vs),662(m,sh),655(w,sh),612(w), 454(vs,sh),447(vs),385(vw),365(vw,sh), 302(w,sh),285(m)
$[(C_6H_5)_3Sb(Cl)]_2O$ Nujol	3044(w),1968(vw),1891(vw),1824(vw), 1780(vw),1659(vw),1578(w),1482(s), 1444(s,sh),1436(vs),1334(w),1307(w), 1244(vw),1177(m),1153(w),1058(m), 1018(m),996(s),913(w),851(vw), 840(vw),768(vs),744(s),731(vs), 690(vs),661(vw),653(vw),611(w), 456(s),448(s),388(vw),305(w,sh), 290(m),280(m,sh)

Table 1 (cont'd)

$[(C_6H_5)_3Sb(ONO_2)]_2O$ Kel-F, Nujol	3045(w),2240(w),1950(vw),1885(vw), 1815(vw),1660(vw),1575(w),1510(m,sh), 1492(vs),1475(m),1432(s),1335(w), 1305(w,sh),1280(vs),1183(w),1160(vw), 1064(m),1020(m),995(s),975(vs), 915(vw),840(vw),802(w),740(vs), 708(vs),690(vs),455(vs),445(s,sh), 380(m),300(w,sh),280(w,b)
$(C_6H_5)_3SbO$ Nujol	3065(w,sh),3045(m),1945(vw),1878(w), 1808(w),1760(vw),1570(w),1478(s), 1430(vs),1330(vw),1305(w),1260(vw), 1178(vw),1155(vw),1074(s),1063(m), 1022(s),998(s),967(vw),917(w), 850(vw),743(vs),728(vs),693(vs), 660(vs,b),617(w),463(s),447(vs), 305(m,sh),295(m),278(m)
$(C_6H_5)_3SbO \cdot 0.3\ H_2O$ Nujol	3135(vw),3065(m,sh),3045(m),1950(vw), 1890(vw),1825(w),1575(m),1473(s), 1430(s),1330(m),1302(m),1265(vw), 1180(s),1158(w),1065(vs),1021(m), 998(m),980(w),860(w),850(vw,sh), 733(vs),695(vs),655(vs),616(w), 475(vs),450(vs),300(m),278(m)
Sb_2O_3 Nujol	960(vw,b),740(vs)

[a] s, strong; m, medium; w, weak; sh, shoulder; b, broad; d, doublet; v, very.

resonance analytical spectrometer Model A60-A. Most spectra were obtained by sweeping slowly through the field and interchanging the reference with the sample being studied. In these cases, acetaldehyde or tetramethylsilane were used as external references. The sample peaks and the reference peaks are obtained on the same spectrum thereby facilitating the calculation of the chemical shifts in approximate τ values. Methylene proton shifts in compounds containing n-propyl and n-butyl groups and phenyl proton shifts are recorded as ranges.

For most compounds containing phenyl groups, the spectra were also obtained using benzene as an internal standard. This facilitates calculation of chemical shifts of the phenyl protons from the benzene signal and thereby enables one to observe the relative electron withdrawing or electron donating ability of the group to which the phenyl ring is attached. Proton magnetic resonance data are listed in Table 7; and Figure 68 shows a schematic diagram of the phenyl proton shifts with respect to benzene.

X-ray powder spectra

The x-ray powder spectra were obtained with a Norelco X-ray Generator, type 12045, using a wide range goniometer and a proportional detector. A copper target was used with K_α Line at 1.541 Å. A nickel filter was used.

Manipulative methods

All solvents were stored and transferred in an inert atmosphere box (D. L. Herring Dri-Lab and Dri-Train combination) containing dry nitrogen. All glass apparatus was baked at 150°C. and moved into the dry box while still hot or else was flamed dry while evacuated. Most chloraminations were carried out on a vacuum line similar to that shown in Figure 1, which was flamed before every reaction. The ether used was peroxide-free.

The anhydrous ether solution of ammonia-free chloramine was introduced into a special tube flask in vacuo. The flask was equipped with a vacuum line adapter to insure that the solution was never exposed to the atmosphere before being used. The solution was then distilled onto the stibine taking care to leave the last drop or two to avoid decomposition of the chloramine. It has been demonstrated in this laboratory that the majority of the chloramine does not distill until about the last five milliliters. This is clearly shown by curves A and B of Figure 2 in which a forty milliliter sample of 0.054 M chloramine was distilled to the last 0.1 milliliter. The progress of the distillation was followed by collecting each five milliliters of distillate and determining the millimoles of chloramine in that individual increment. These results are shown by curve A. The total millimoles of chloramine distilled,

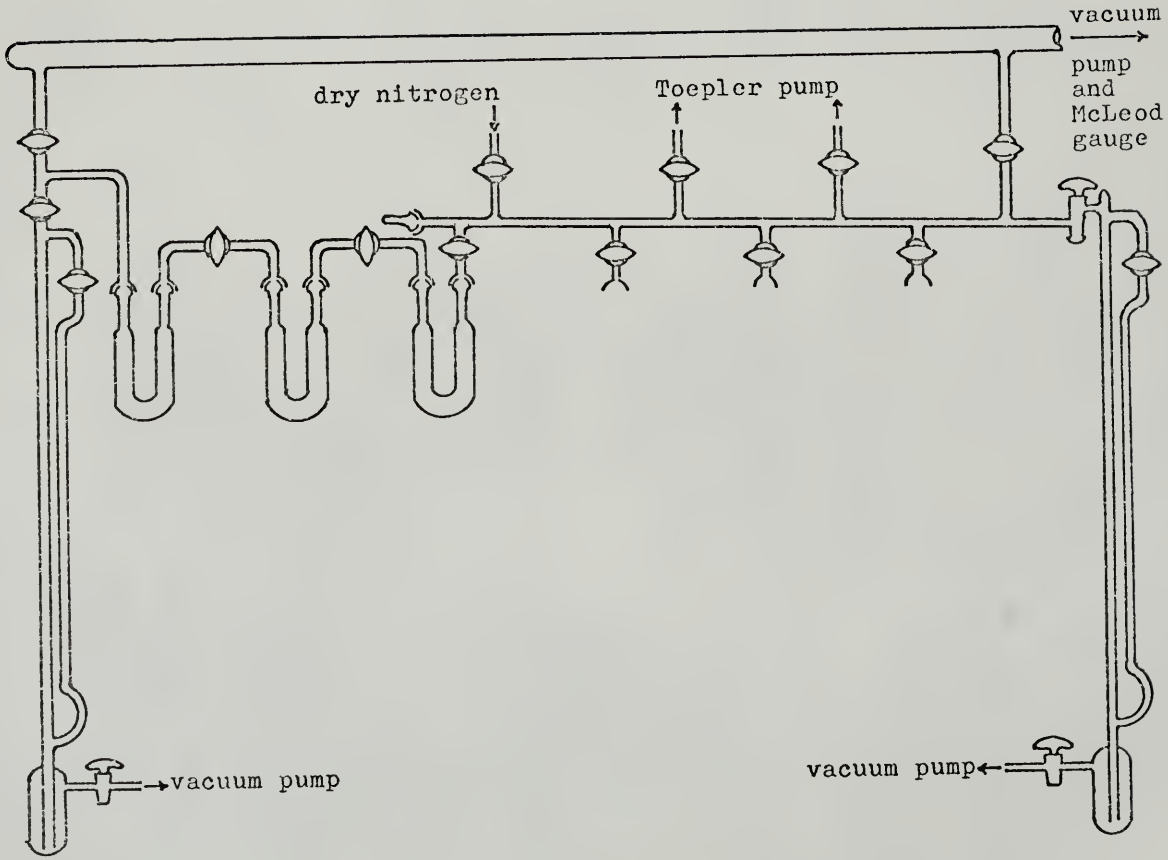


Fig. 1.-Vacuum line.

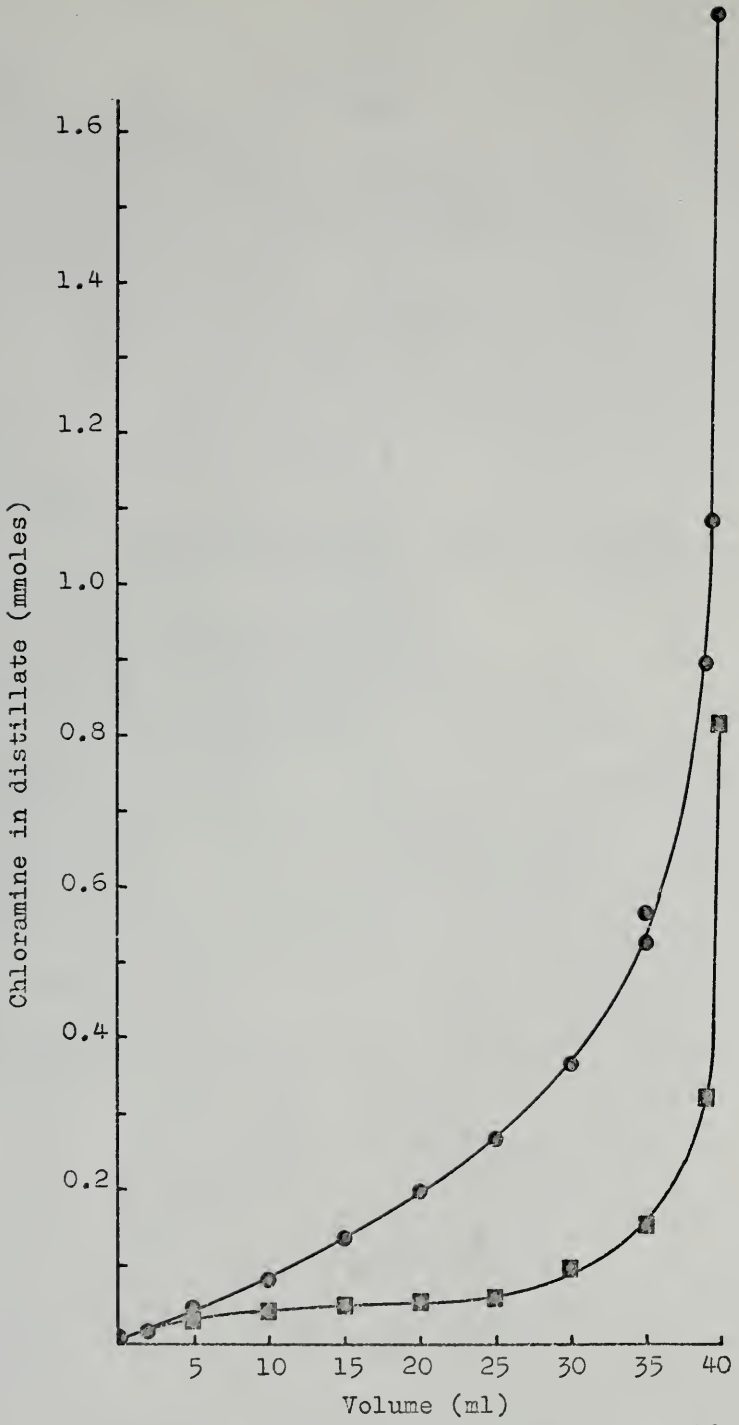


Fig. 2.-Distillation curve for ammonia-free chloramine.

which was obtained by the addition of all the preceding increments, is represented by curve B.

Chloramine decomposes to some extent during the filtration through anhydrous copper sulfate and during the distillation process. Yields of ammonia-free chloramine ranging from 40 to 70 per cent have been obtained by the process described above. The factors which influence the decomposition process are not well understood. However, it is possible that the decomposition is facilitated by minute particles of anhydrous copper sulfate that come through the glass frit during the filtration, since freshly distilled ammonia-free chloramine can be redistilled to dryness with a 90 to 95 per cent recovery of chloramine in the distillate.

Synthesis of trialkylstibines

Trialkyl- and triarylstibines generally have been prepared by the Grignard method (8,9,15). Recently, Stamm and Breindel (16) discovered a novel method for the preparation of the trialkylstibines using antimony(III) oxide and the appropriate trialkylaluminum. However, they did not report the preparation of trimethyl- or tri-n-propylstibines. We have applied their method to these compounds. The reactions were always carried out in a dry box and the trialkylaluminum reagent was not distilled before use.

Trimethylstibine and trimethyldibromostibane

$$3(CH_3)_3Al + Sb_2O_3 \rightarrow 2(CH_3)_3Sb + 3CH_3AlO$$

A n-hexane solution of trimethylaluminum, 0.3 mole, was added dropwise with vigorous stirring to a n-hexane slurry of antimony(III) oxide, 0.1 mole. The total n-hexane used was 100 milliliters and the addition took approximately five hours. After the addition was complete, the contents of the flask were heated to 60°C. for an additional two hours and then allowed to cool over night. Efficient stirring is a critical factor in this reaction.

The volatile material was distilled at atmospheric pressure and the fraction boiling under 80°C. was then treated with a carbon tetrachloride solution of bromine. This produced 49.7 grams of trimethyldibromostibane which melted at 185-186.5°C. (dec.) [Lit. (17) m.p. 200°C.]. The yield based on antimony(III) oxide was 76 per cent of theory.

The infrared spectrum of trimethyldibromostibane is shown in Figure 3.

No analytical data were obtained as this is a well characterized compound (13,17).

The proton magnetic resonance spectrum of trimethyldibromostibane is shown in Figure 4. The spectrum consists of one peak which is attributed to the methyl protons. The chemical shift value is listed in Table 7.

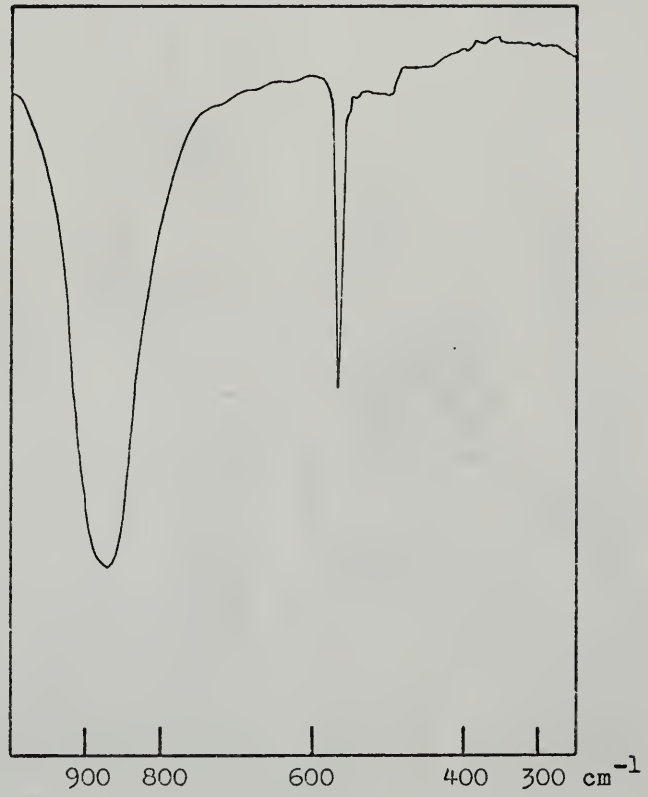


Fig. 3.-Infrared spectrum of $(CH_3)_3SbBr_2$.

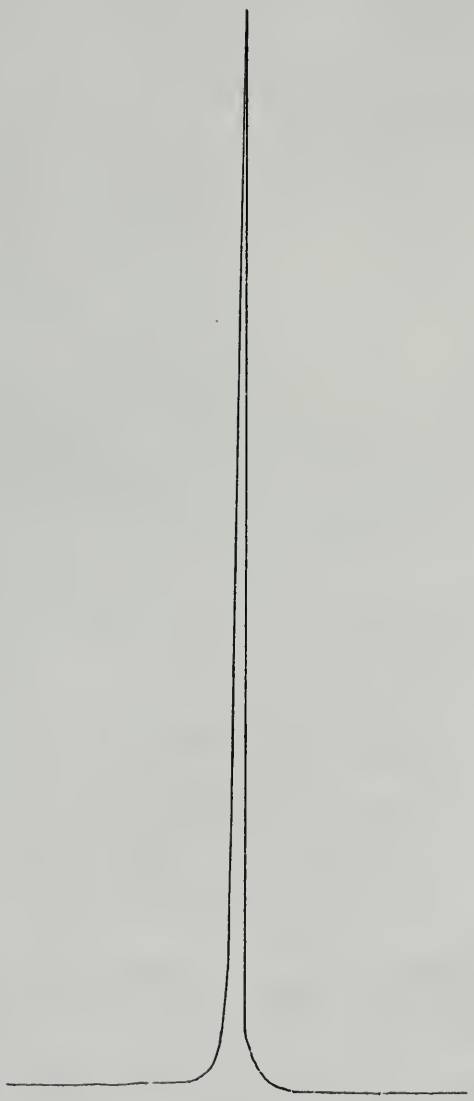


Fig. 4.-Proton magnetic resonance spectrum of $(CH_3)_3SbBr_2$.

Trimethylstibine is obtained from the dibromo compound in low yield by reacting it with powdered zinc (18) in an oxygen-free system. Trimethylstibine boils at 80-81°C. at 763 mm.

The infrared spectrum of trimethylstibine is shown in Figure 5.

The proton magnetic resonance spectrum was not obtained.

Tri-n-propylstibine

$$3(n\text{-}C_3H_7)_3Al + Sb_2O_3 \rightarrow 2(n\text{-}C_3H_7)_3Sb + 3n\text{-}C_3H_7AlO$$

Tri-n-propylaluminum was reacted with antimony(III) oxide in the same manner as that described for trimethylstibine. Upon completion of the initial reaction, the n-hexane was removed by atmospheric distillation and then tri-n-propylstibine was vacuum distilled from the reaction flask. Tri-n-propylstibine boils at 93-95°C. at 15.5 mm [Lit. (19) b.p. 113°C. (39 mm)]. The yield was 41 per cent of theory based on the above equation.

Figure 6 shows the infrared spectrum of tri-n-propylstibine.

The proton magnetic resonance spectrum of tri-n-propylstibine was not obtained.

Triethylstibine

$$3(C_2H_5)_3Al + Sb_2O_3 \rightarrow 2(C_2H_5)_3Sb + 3C_2H_5AlO$$

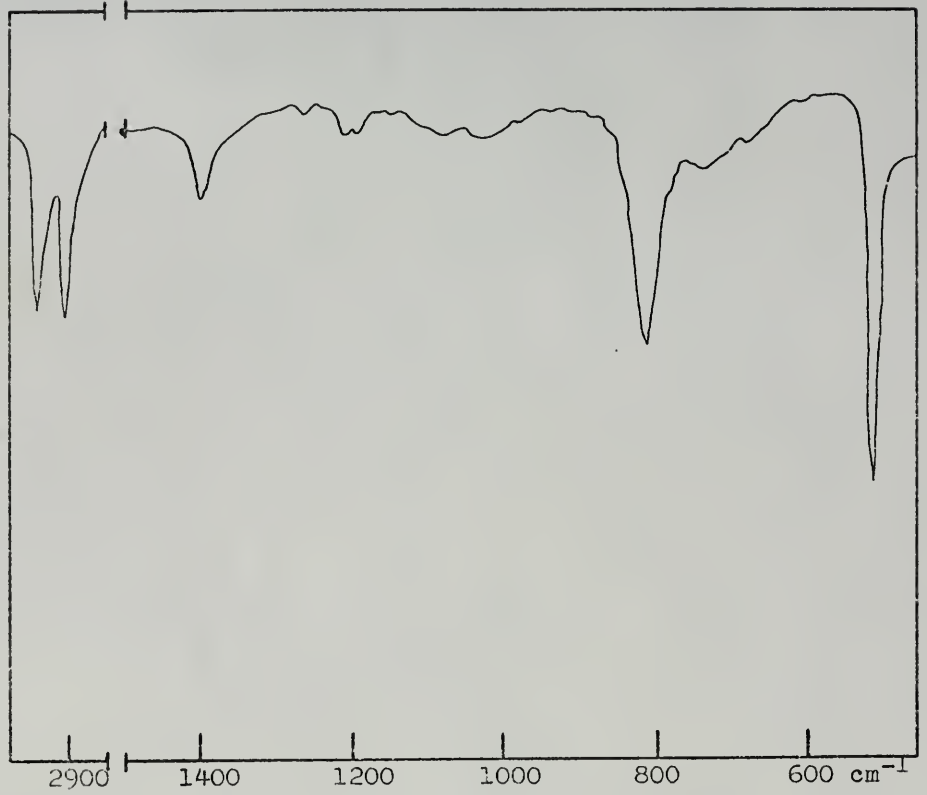


Fig. 5.-Infrared spectrum of $(CH_3)_3Sb$.

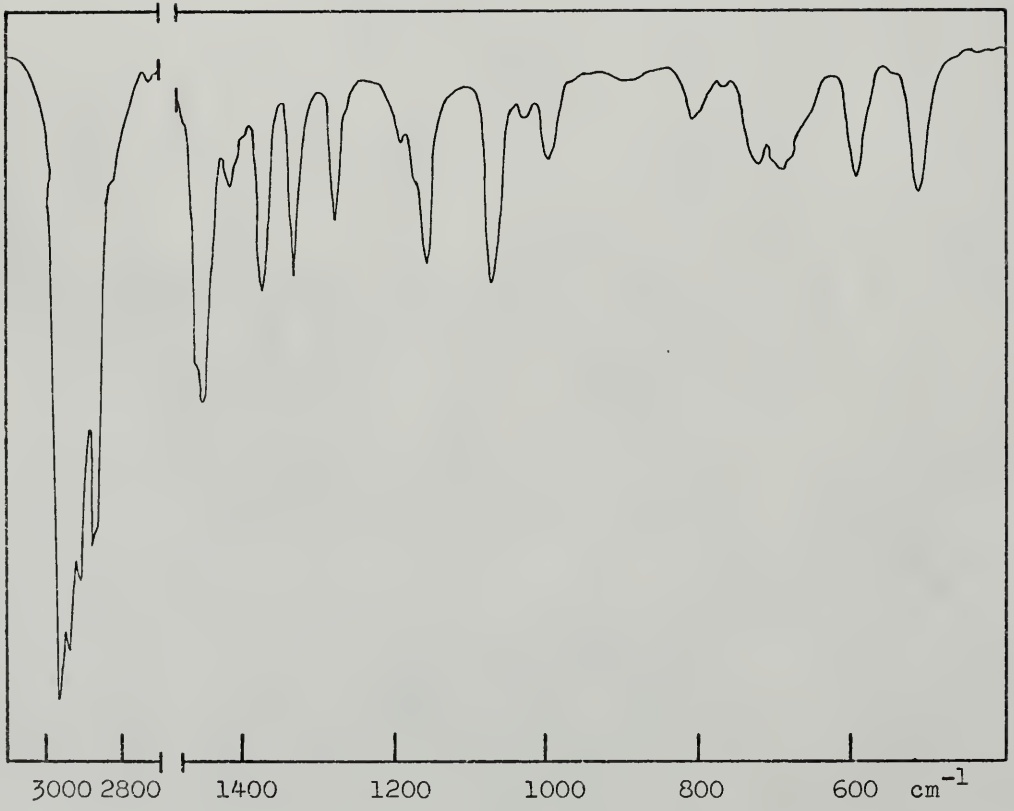


Fig. 6.-Infrared spectrum of $(\underline{n}\text{-}C_3H_7)_3Sb$.

Triethylstibine was prepared by the method of Stamm and Breindel (16) and worked up in the same manner as that described for tri-n-propylstibine.

The infrared spectrum of triethylstibine is shown in Figure 7.

The proton magnetic resonance spectrum of triethylstibine was not obtained.

Ammonia-free chloramination of some trialkylstibines and triphenylstibine

Trialkylstibines and triphenylstibine react with ammonia-free chloramine to form iminobis-(trialkylchlorostibanes) and iminobis-(triphenylchlorostibane). The reaction is thought to proceed according to the following equations:

$$R_3Sb + NH_2Cl \rightarrow R_3Sb(NH_2)Cl$$

$$2R_3Sb(NH_2)Cl \rightarrow [R_3Sb(Cl)]_2NH + NH_3$$

A side reaction is observed in certain cases in which trialkyl- or triphenyldichlorostibane is produced in variable yields. This reaction is thought to proceed according to the following equation:

$$R_3Sb(NH_2)Cl + NH_2Cl \rightarrow R_3SbCl_2 + 1/3N_2 + 4/3NH_3$$

Iminobis-(trimethylchlorostibane)

$$2(CH_3)_3Sb + 2NH_2Cl \rightarrow [(CH_3)_3Sb(Cl)]_2NH + NH_3$$

$$(CH_3)_3Sb(NH_2)Cl + NH_2Cl \rightarrow (CH_3)_3SbCl_2 + 1/3N_2 + 4/3NH_3$$

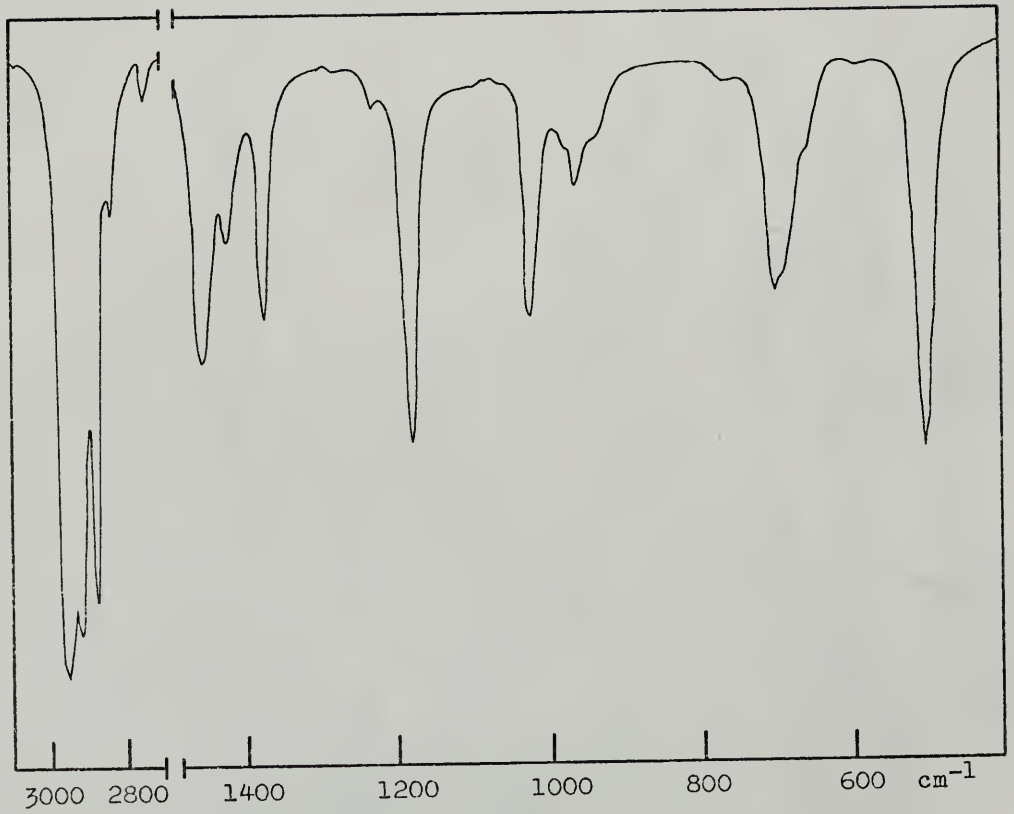


Fig. 7.-Infrared spectrum of $(C_2H_5)_3Sb$.

Trimethylstibine, 4.49 mmoles, was distilled from calcium hydride into a tube flask equipped with a stirring bar. Twenty-seven milliliters of a 0.19 molar ethereal solution of chloramine was then slowly distilled into the flask with stirring. The temperature was maintained at -78°C. throughout the transfer, and reaction was evident. The solid and solvent became yellow and gas evolution was noticeable as the flask was warmed to room temperature. The flask was maintained at this temperature for 80 minutes, after which the ether was removed by distillation. The non-condensible gas formed during the reaction was estimated to be less than 0.5 mmole. The ether was treated with gaseous hydrogen chloride, which produced 0.17 gram of ammonium chloride. This corresponds to 3.18 mmoles of ammonia. No unreacted trimethylstibine was detected. This indicates that chloramine was in excess and explains why more ammonium chloride was found than theory predicts.

The sealed flask was transferred to a dry box and the crude product, 0.98 gram, was treated with four 5 milliliter portions of boiling toluene. The insoluble solid (A) was dried in vacuo. Product (A) decomposed to a metallic gray solid and a volatile reactive liquid when heated above 200°C., and readily evolved ammonia when exposed to the atmosphere. The yield was 0.67 gram which was 71 per cent of theory based on the above equations.

Iminobis-(trimethylchlorostibane) is slightly soluble in chloroform and boiling toluene and insoluble in a variety of other organic solvents. The infrared spectrum of iminobis-(trimethylchlorostibane) is shown in Figure 8.

Anal. of product (A). Calcd. for $[(CH_3)_3Sb(Cl)]_2NH$: C, 17.17; H, 4.56; N, 3.34; Sb, 58.05; Cl, 16.90. Found: C, 18.13; H, 4.79; N, 3.69; Sb, 58.81; Cl, 17.14.

The toluene wash liquid was evaporated to dryness leaving 0.27 gram of a white solid (B) as residue. The material decomposed around 220°C. Product (B) appears to be a mixture of trimethyldichlorostibane (64.4 per cent), melting point 230°C. (dec.), and iminobis-(trimethylchlorostibane) (35.6 per cent) which decomposes at temperatures above 200°C. The infrared spectrum was consistent with this assumption. The total yield of trimethyldichlorostibane was 16.2 per cent of theory. The iminobis-(trimethylchlorostibane) in the above mixture is difficult to separate and separation is not feasible in most cases. The combined amounts of the imino compound in products (A) and (B) corresponds to a total yield of 81.2 per cent of theory.

The proton magnetic resonance spectrum of iminobis-(trimethylchlorostibane) is shown in Figure 9. The complexity of the spectrum probably results from complex formation with the chloroform which was used as solvent. A peak resulting from the proton on the nitrogen could not be found.

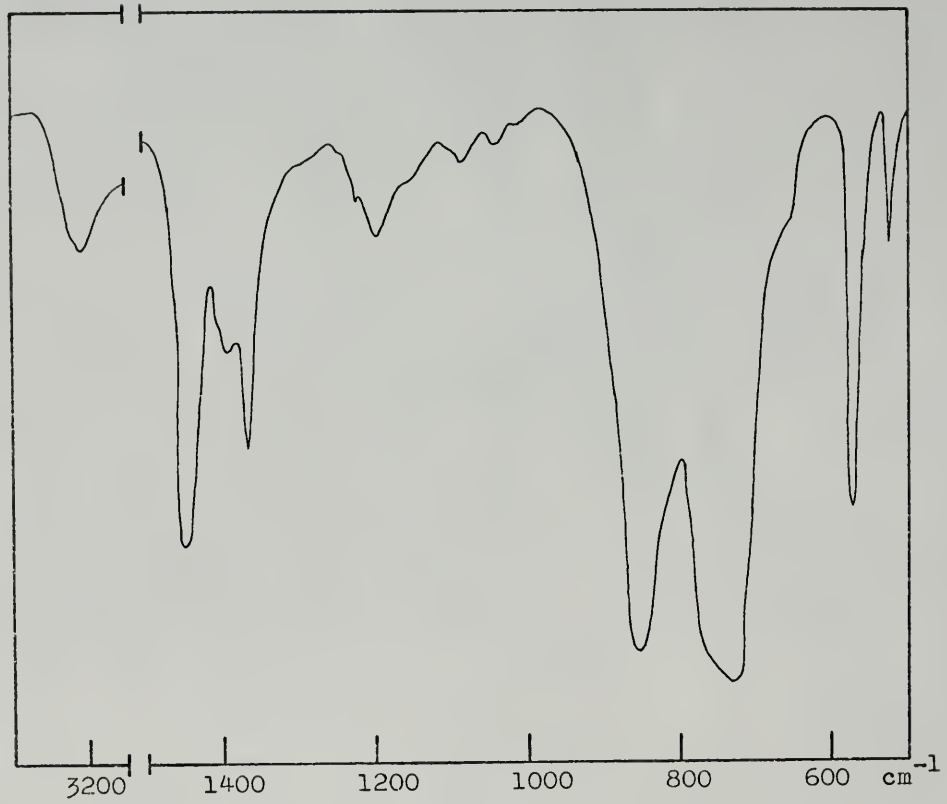


Fig. 8.-Infrared spectrum of $[(CH_3)_3Sb(Cl)]_2NH$.

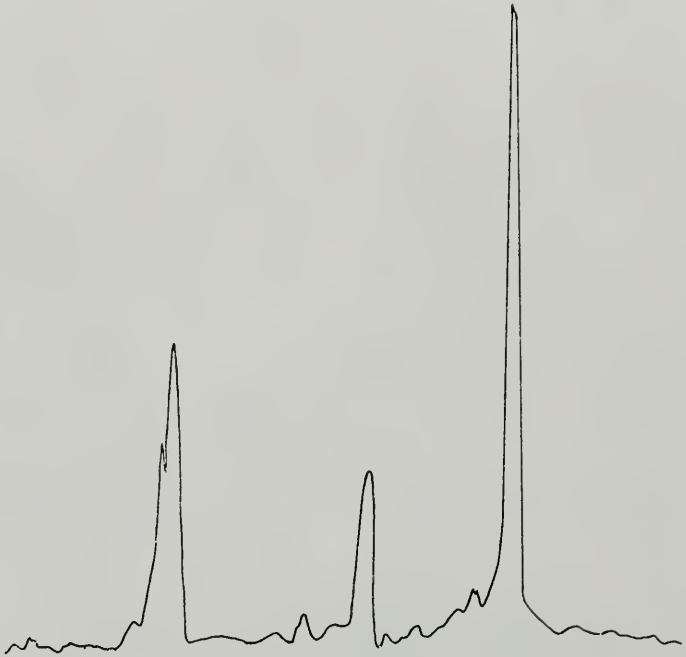


Fig. 9.-Proton magnetic resonance spectrum of $[(CH_3)_3Sb(Cl)]_2NH$.

Low-temperature reaction of trimethylstibine with ammonia-free chloramine

Trimethylstibine, 2.1 mmoles, was distilled from calcium hydride into the vacuum line. Five milliliters of a 0.45 molar ethereal solution of chloramine was condensed onto the stibine at -78°C. and allowed to react at this temperature for three hours. The temperature was then allowed to rise to -45°C. at which time the volatile material, which includes any ammonia produced by a condensation reaction, was removed. Dry toluene was condensed onto the residual white solid at -78°C. and then 4.2 mmoles of dry hydrogen chloride gas was condensed into the flask. The contents of the flask were stirred for one hour at this temperature and then allowed to come to room temperature. The volatile material was removed from the flask by vacuum and fractionated. A total of 0.92 mmole of gaseous hydrogen chloride was consumed in the reaction.

The residue in the reaction flask weighed approximately 0.13 gram. Analysis of this solid gave an Sb:N:Cl ratio of 1.9:1.0:5.1. Therefore the material that reacted with gaseous hydrogen chloride must be some species with the same Sb:N:Cl ratio as iminobis-(trimethylchlorostibane), but not necessarily this compound. The reaction might proceed according to an equation similar to the following:

$$[(CH_3)_3Sb(Cl)]_2NH_{(s)} + 3HCl_{(g)} \rightarrow 2(CH_3)_3SbCl_{2(s)} + NH_4Cl_{(s)}$$

Sb:N:Cl ratio in product mixture: 2:1:5

Had the reactive species been $(CH_3)_3Sb(NH_2)Cl$, the Sb:N:Cl ratio would have been 1:1:3.

The unreacted stibine was accounted for as trimethylstibine oxide.

Iminobis-(triethylchlorostibane)

$$2(C_2H_5)_3Sb + 2NH_2Cl \rightarrow [(C_2H_5)_3Sb(Cl)]_2NH + NH_3$$

Triethylstibine, 3.1 mmoles, was introduced into a vacuum line and degassed twice. Fifty milliliters of a 0.13 molar ethereal solution of chloramine was slowly transferred onto the stibine with stirring at -78°C. The material was warmed to room temperature and stirred for two hours. During this time a white solid formed. The solvent was removed from the flask by vacuum and the sealed apparatus was transferred into an inert atmosphere box. The crude material was washed with several small portions of hot cyclohexane and dried in vacuum. The material melted at 126-129°C. to a clear liquid. A total of 0.64 gram was obtained which was 87 per cent of theory based on the above equation.

Iminobis-(triethylchlorostibane) is soluble in hot benzene and chloroform and is insoluble in ethyl and iso-

propyl ethers, n-hexane and cyclohexane. The melting point can be improved to 128-129°C. by recrystallization from benzene, but a large portion of the compound is decomposed in the process. Figure 10 shows the infrared spectrum of iminobis-(triethylchlorostibane).

Anal. Calcd. for $[(C_2H_5)_3Sb(Cl)]_2NH$: C, 28.61; H, 6.20; N, 2.78; Sb, 48.33; Cl, 14.08; MW, 504. Found: C, 28.81; H, 6.12; N, 2.73; Sb, 48.16; Cl, 14.31; MW, 412.

The proton magnetic resonance spectrum of iminobis-(triethylchlorostibane) is shown in Figure 11. Peak A results from the protons of the methylene group, peak A' from the protons of the methylene group of the hydrolysis product (hydrolysis was brought about by water in the deutero-chloroform), and peak B from the protons of the methyl group. The methyl protons of the hydrolysis product are hidden under peak B. The imino proton peak could not be resolved.

Iminobis-(tri-n-propylchlorostibane)

$$2(n\text{-}C_3H_7)_3Sb + 2NH_2Cl \rightarrow [(n\text{-}C_3H_7)_3Sb(Cl)]_2NH + NH_3$$

Tri-n-propylstibine, 2.4 mmoles, was introduced into a vacuum line and degassed twice. Forty milliliters of a 0.07 molar ethereal solution of chloramine was slowly condensed onto the stibine with stirring at -78°C. The liquid was stirred at this temperature for one hour and then warmed

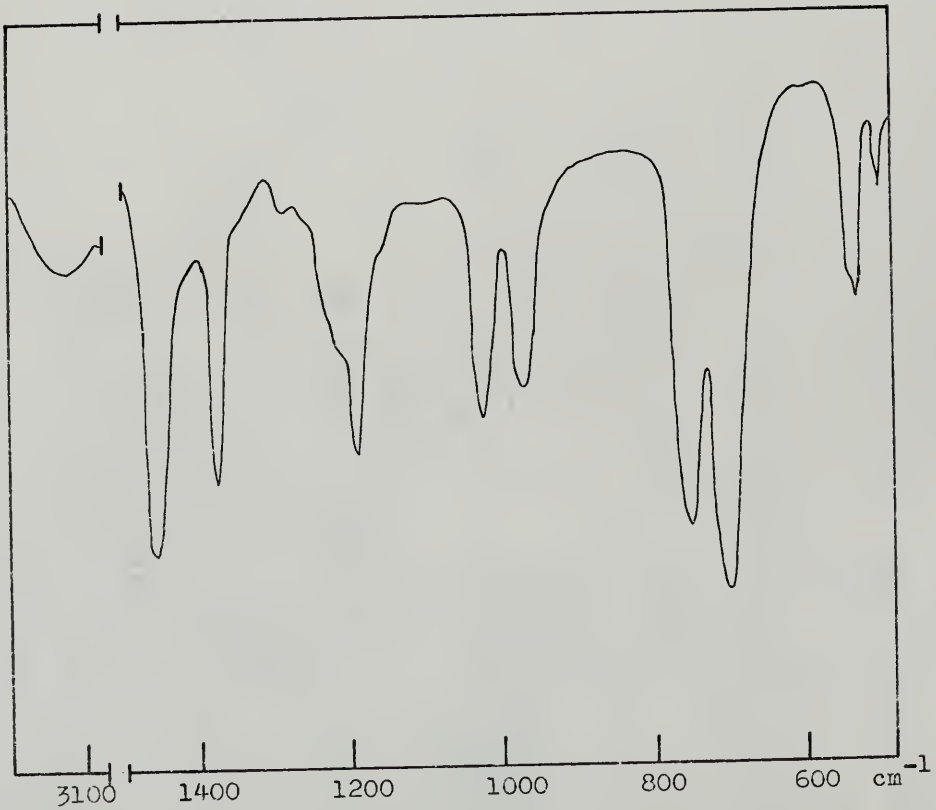


Fig. 10.-Infrared spectrum of $[(C_2H_5)_3Sb(Cl)]_2NH$.

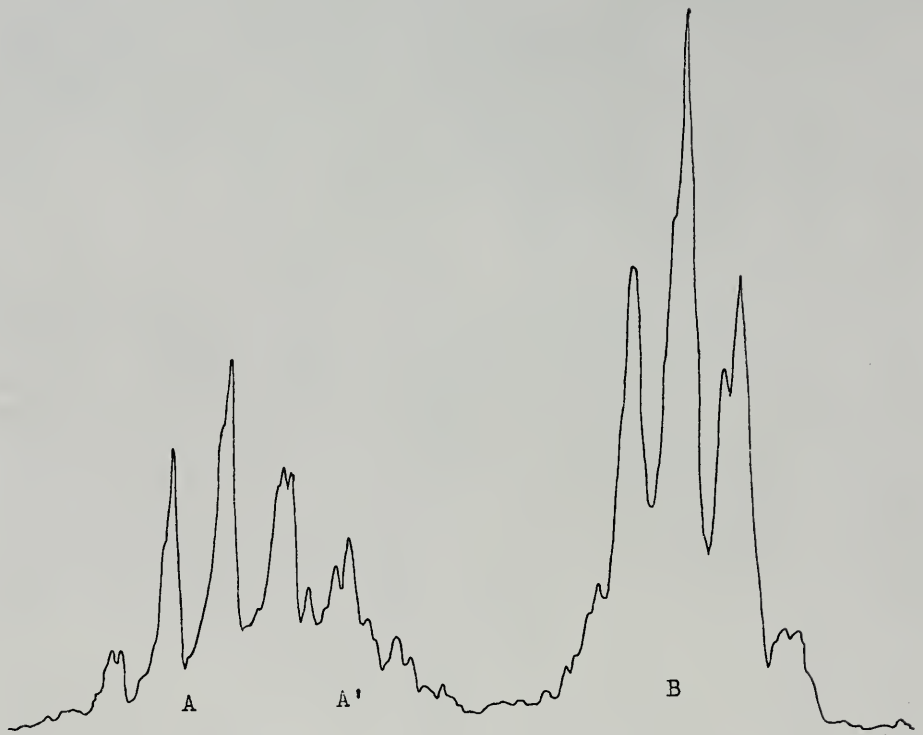


Fig. 11.-Proton magnetic resonance spectrum of $[(C_2H_5)_3Sb(Cl)]_2NH$.

to room temperature and allowed to react for an additional two hours. The reaction product was soluble in ether at room temperature. The solvent was removed by vacuum and the sealed flask was transferred into an inert atmosphere box. The crude product was washed with several small portions of n-hexane and dried by vacuum. The yield was 0.51 gram of a white solid (72 per cent of theory). The unrecrystallized solid melted at 87-94°C. Low temperature recrystallization from ether yields a material which melts at 83-85°C. The wash solvent yielded an additional portion of product which raised the yield to 76.5 per cent of theory based on the above equation.

Iminobis-(tri-n-propylchlorostibane) is soluble in ethyl ether and chloroform and slightly soluble in n-hexane. Heating the compound in various solvents causes decomposition and the formation of an oil. The infrared spectra of the crude and recrystallized product are very similar and the spectrum of the latter is shown in Figure 12.

Anal. Calcd. for $[(n\text{-}C_3H_7)_3Sb(Cl)]_2NH$: C, 36.77; H, 7.37; N, 2.38; Sb, 41.42; Cl, 12.06. Found: (recrystallized) C, 36.58; H, 7.22; N, 2.17; Sb, 42.13; Cl, 11.99; (crude) C, 36.35; H, 7.14; N, 2.67; Sb, 41.29; Cl, 11.69.

Figure 13 shows the proton magnetic resonance spectrum of iminobis-(tri-n-propylchlorostibane). Peak A is attributed to the methylene protons and peak B to the methyl protons. The imino proton could not be resolved.

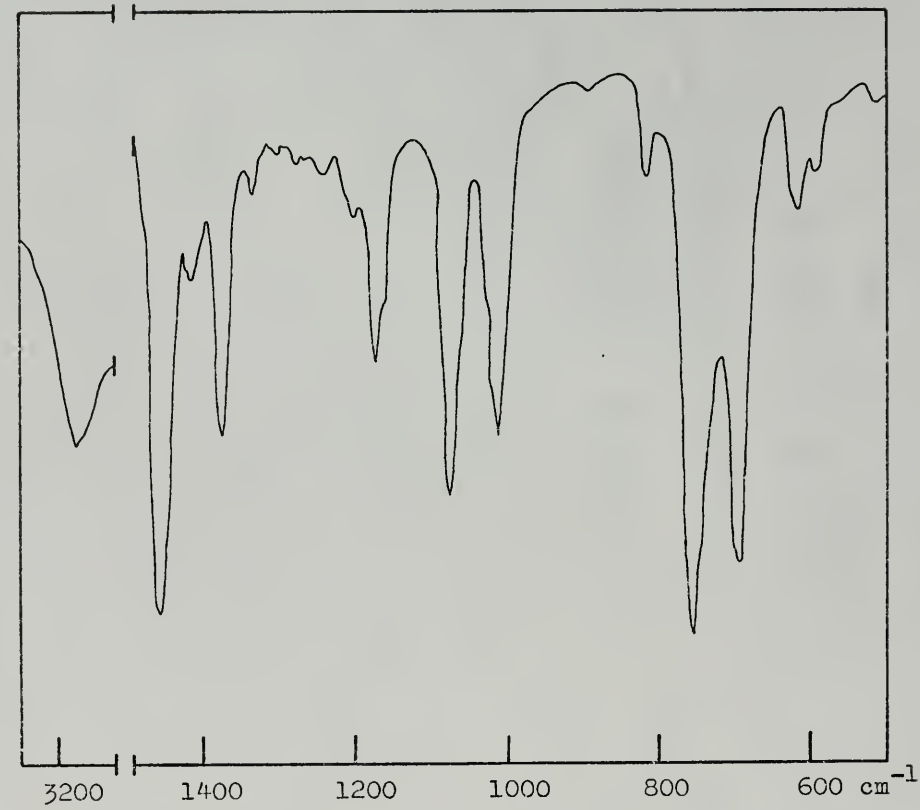


Fig. 12.-Infrared spectrum of $[(\underline{n}\text{-}C_3H_7)_3Sb(Cl)]_2NH$.

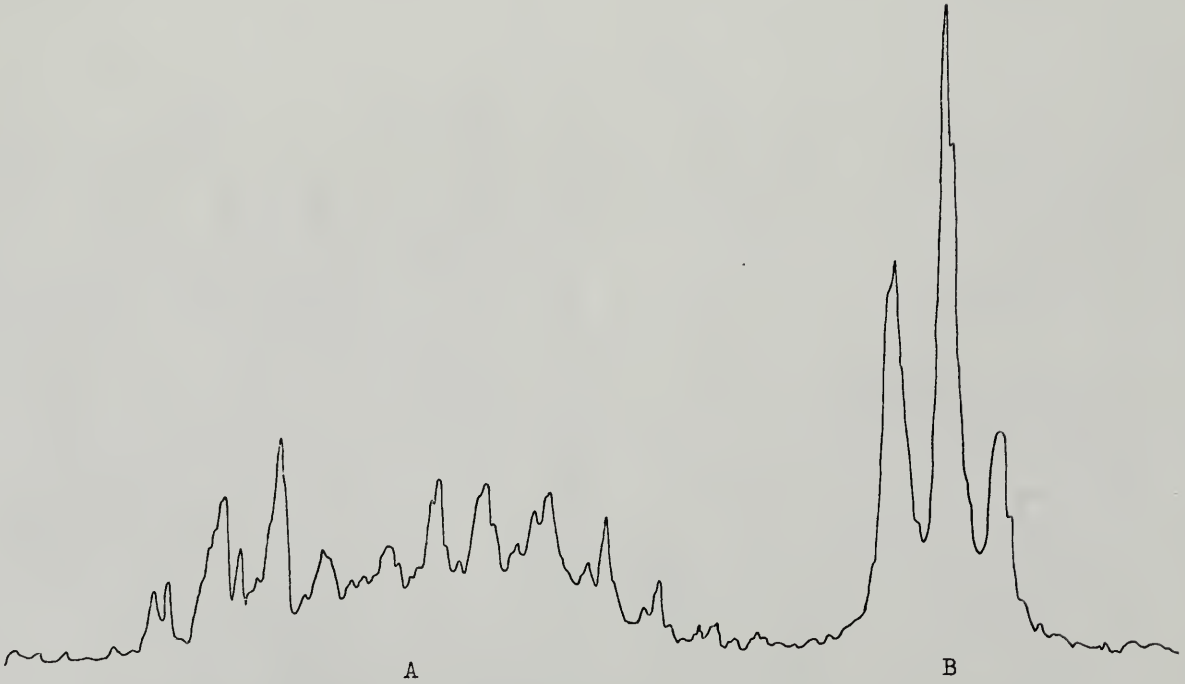


Fig. 13.-Proton magnetic resonance spectrum of $[(\underline{n}\text{-}C_3H_7)_3Sb(Cl)]_2NH$.

Iminobis-(tri-n-butylchlorostibane)

$$2(n\text{-}C_4H_9)_3Sb + 2NH_2Cl \rightarrow [(n\text{-}C_4H_9)_3Sb(Cl)]_2NH + NH_3$$

The effluent gases from the chloramine generator (20) were passed directly through pure tri-n-butylstibine, 0.1 mole, for 1.4 hours. The temperature of the liquid rose to about 60°C. during this period and it became very viscous. The liquid was filtered and stirred under vacuum for twelve hours during which time a gas was evolved and the material partially solidified. The semi-solid substance was spread between two porous plates in a dry inert atmosphere and ground for about fifteen minutes. This process was repeated until a flaky white solid was obtained which melted at 49-50°C. The total yield was 17.7 grams which was 51 per cent of theory based on the above equation.

Vacuum-line technique using ammonia-free chloramine yields the same product in about 90 per cent yield. However, the presence of unreacted stibine causes the formation of an oil from which the product is not readily separated. The infrared spectrum of the oil is consistent with that to be expected for the above product diluted with starting material.

Iminobis-(tri-n-butylchlorostibane) is soluble in most of the common organic solvents. The material cannot be stored for long periods of time as it slowly decomposes to a yellow oil. The infrared spectrum of iminobis-(tri-

n-butylchlorostibane) is shown in Figure 14. For comparison the infrared spectrum of tri-n-butylstibine is shown in Figure 15.

Anal. Calcd. for $[(n\text{-}C_4H_9)_3Sb(Cl)]_2NH$: C, 42.88; H, 8.25; N, 2.08; Sb, 36.23; Cl, 10.55; MW, 672. Found: C, 42.72; H, 8.13; N, 1.80; Sb, 36.24; Cl, 10.51; MW, 549.

Figure 16 shows the proton magnetic resonance spectrum of iminobis-(tri-n-butylchlorostibane). Peak A results from all the methylene protons and peak B from the methyl protons. The absorption resulting from the lone imino proton was not found. The proton magnetic resonance spectrum of tri-n-butylstibine is shown in Figure 17.

Iminobis-(triphenylchlorostibane)

$$2(C_6H_5)_3Sb + 2NH_2Cl \rightarrow [(C_6H_5)_3Sb(Cl)]_2NH + NH_3$$

$$(C_6H_5)_3Sb(NH_2)Cl + NH_2Cl \rightarrow (C_6H_5)_3SbCl_2 + 1/3N_2 + 4/3NH_3$$

In a typical experiment, 39 milliliters of 0.025 M ammonia-free chloramine was condensed into an ethereal solution (50 ml) of 2.14 mmoles of triphenylstibine at liquid nitrogen temperature, and the temperature of the mixture allowed to rise. A white solid formed and the ether became light yellow in color at just under room temperature. Gas evolution was also observed at this point. The reaction was allowed to continue for five hours, after

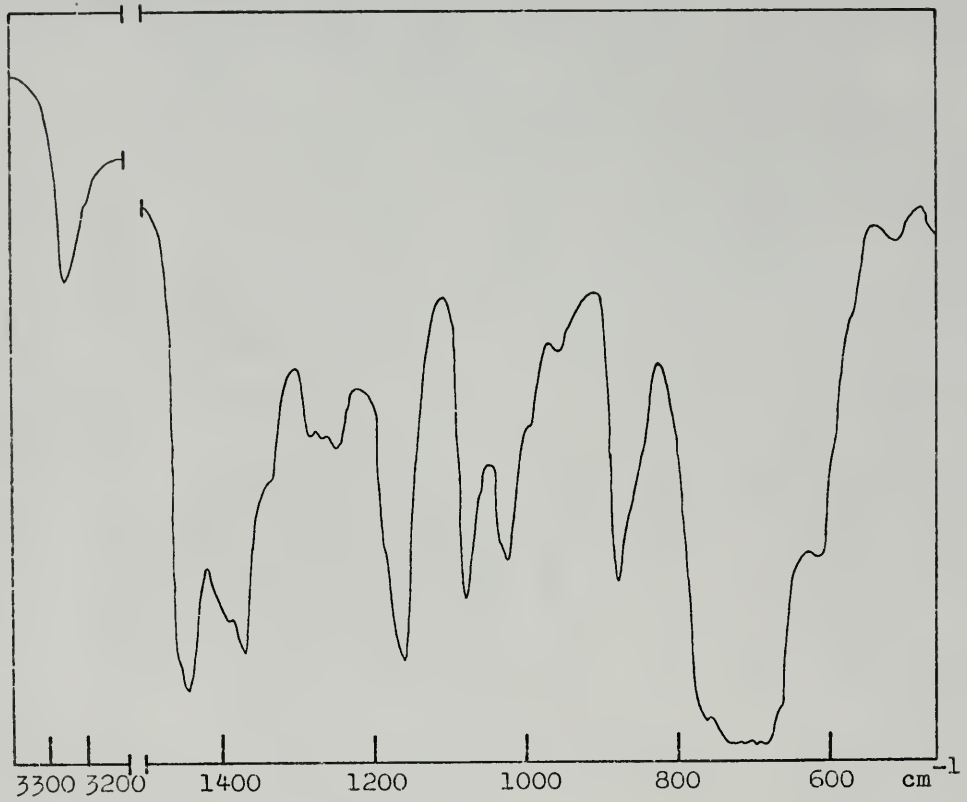


Fig. 14.-Infrared spectrum of $[(\underline{n}\text{-}C_4H_9)_3Sb(Cl)]_2NH$.

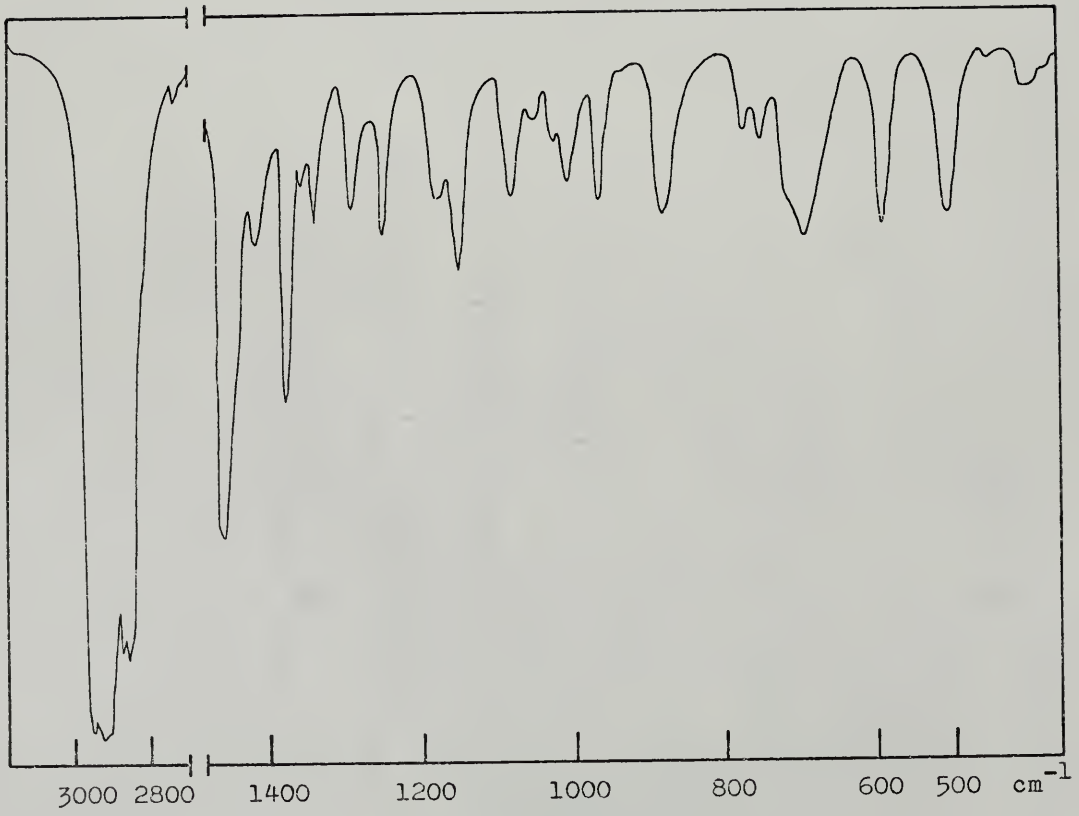


Fig. 15.-Infrared spectrum of $(\underline{n}\text{-}C_4H_9)_3Sb$.

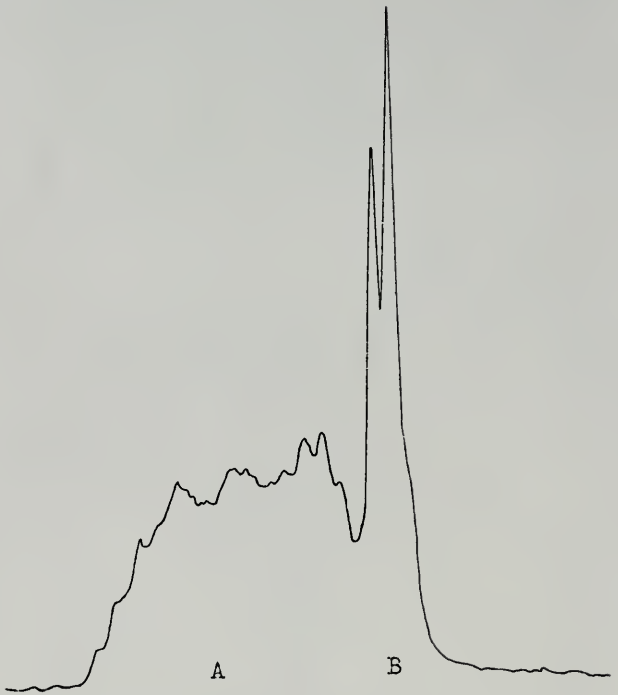


Fig. 16.-Proton magnetic resonance spectrum of $[(\underline{n}\text{-}C_4H_9)_3Sb(Cl)]_2NH$.

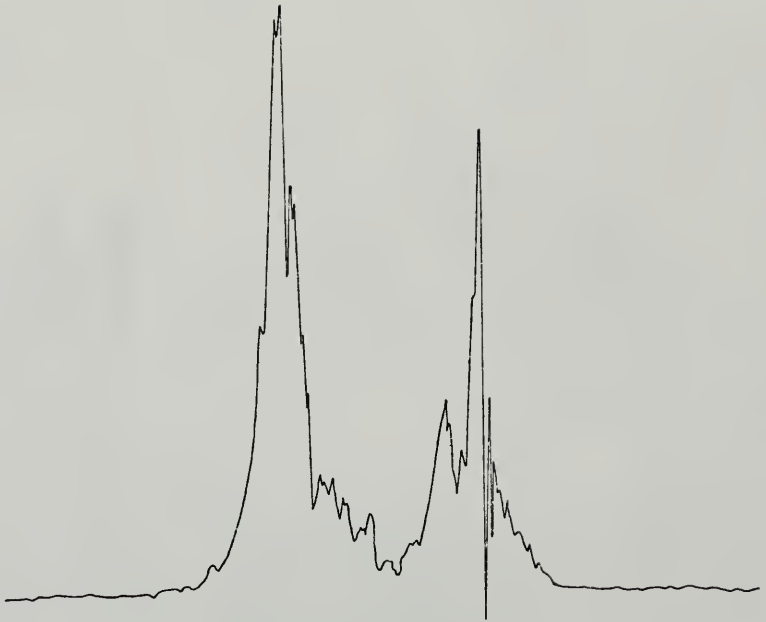


Fig. 17.-Proton magnetic resonance spectrum of $(\underline{n}\text{-}C_4H_9)_3Sb$.

which the solvent was removed by vacuum. A non-condensible gas was formed during the reaction (yield 0.075 mmole). A molecular weight determination showed the gas to be nitrogen. The solvent was then treated with gaseous hydrogen chloride, which produced a total of 1.49 mmoles of ammonium chloride.

The sealed reaction flask was transferred into a dry box and the crude product was washed with 0.5 milliliter portions of dry carbon tetrachloride until the insoluble solid gave a melting point of 219-220.5°C. Yields of iminobis-(triphenylchlorostibane) of 55 to 71 per cent and of triphenyldichlorostibane of 25 to 43 per cent of theory were obtained in a series of experiments using various mole ratios and concentrations of reactants.

Iminobis-(triphenylchlorostibane) is soluble in chloroform and hot benzene and slightly soluble in ether and carbon tetrachloride. It does not react with gaseous or liquid ammonia, nor is it readily susceptible to hydrolysis in the atmosphere in the dry state. The infrared spectrum is shown in Figure 18.

Anal. Calcd. for $[(C_6H_5)_3Sb(Cl)]_2NH$: C, 54.59; H, 3.94; N, 1.77; Cl, 8.95. Found: C, 54.26; H, 4.13; N, 1.81; Cl, 9.15.

The carbon tetrachloride wash liquid was evaporated to dryness leaving 0.35 gram of an oil as residue. The oil was extracted with a small portion of petroleum ether, which

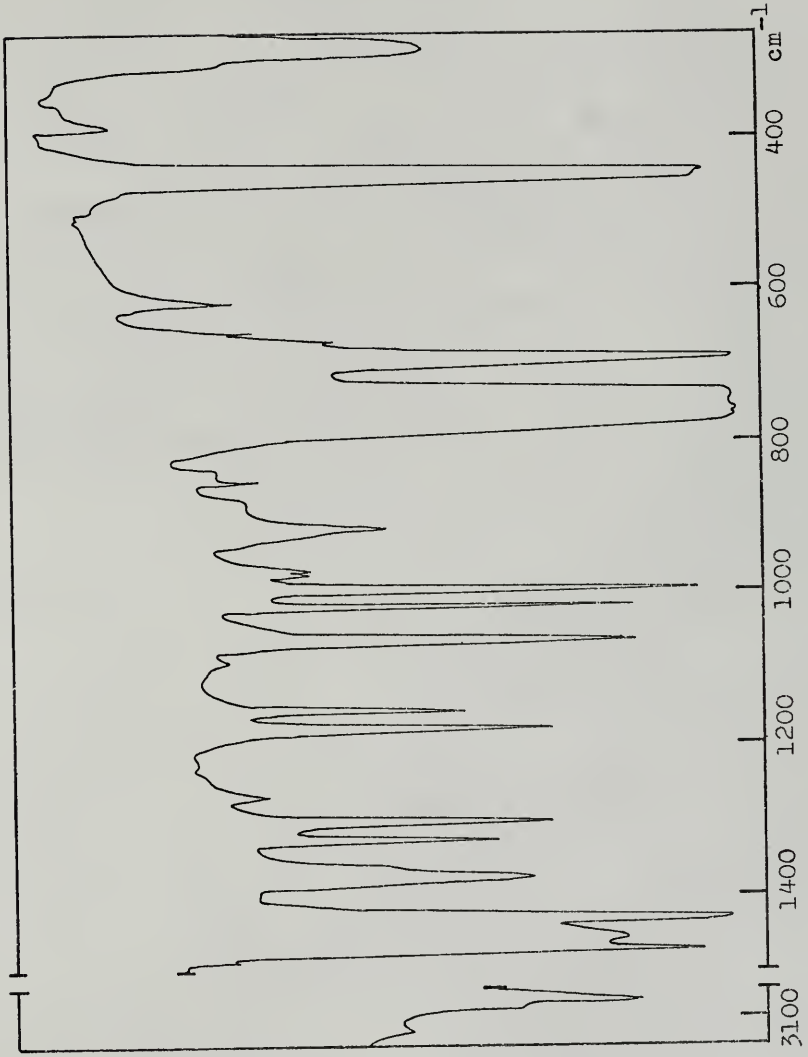


Fig. 18.-Infrared spectrum of $[(C_6H_5)_3Sb(Cl)]_2NH$.

dissolves triphenylstibine. The insoluble residue was identified as triphenyldichlorostibane which melts at 143-144°C. A total of 0.47 mmole was obtained. Triphenylstibine, 0.31 mmole, was recovered from the petroleum ether. The infrared spectra of triphenylstibine and triphenyldichlorostibane are shown in Figures 19 and 20 respectively.

The proton magnetic resonance spectrum of iminobis-(triphenylchlorostibane) is shown in Figure 21. Peaks A and A' are assigned to the phenyl protons; peak A to the ortho protons and peak A' to the meta and para protons. The spectrum was also taken with respect to benzene which was used as an internal standard. The ortho proton signal is shifted -18 cps from the benzene signal, whereas the meta and para proton signals are not significantly changed from benzene. A downfield shift from benzene is recorded as negative values and an upfield shift as positive values. The signal for the imino proton is probably weak and broad and difficult to observe, and in some cases, it is probably overlapped by the phenyl proton absorptions.

The proton magnetic resonance spectrum of triphenylstibine is shown in Figure 22. The chemical shift values for the ortho, meta and para protons are similar and as a result, the ortho proton signal is not significantly moved downfield from that of the meta and para protons. One can see the typical ortho proton pattern of four peaks of

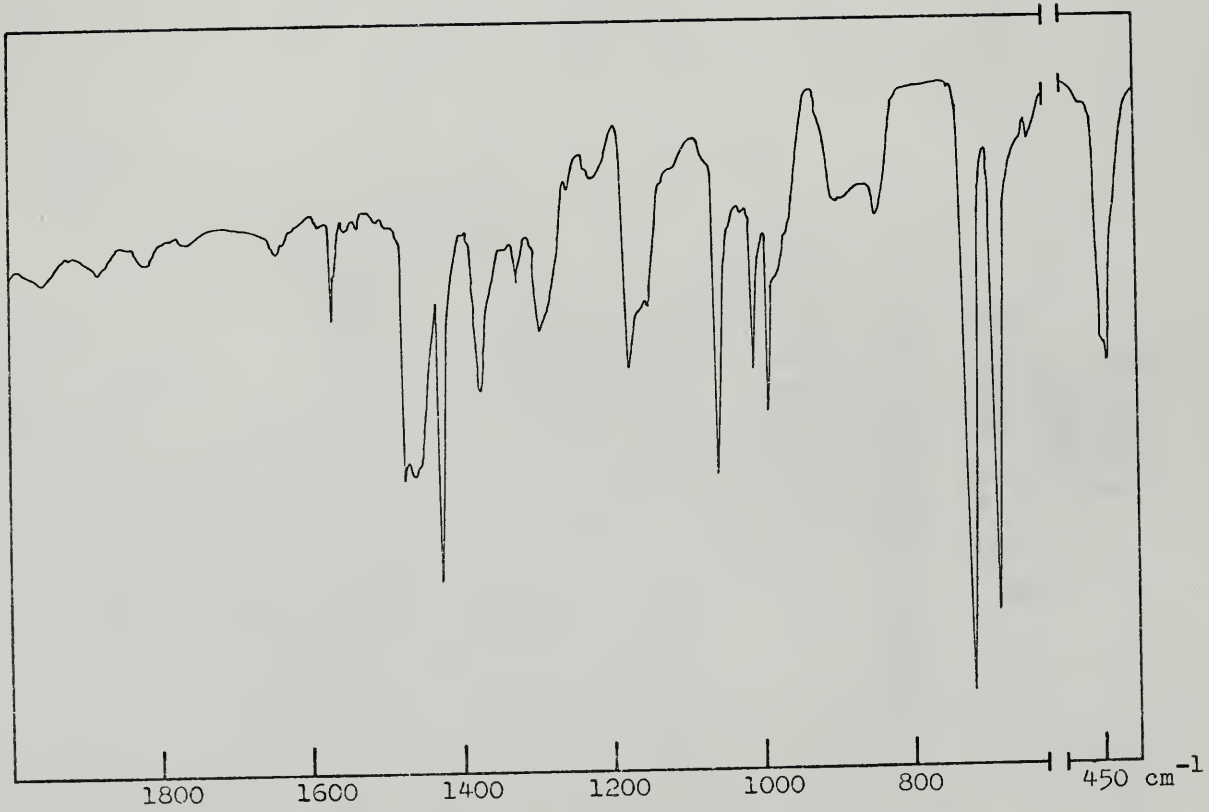


Fig. 19.-Infrared spectrum of $(C_6H_5)_3Sb$.

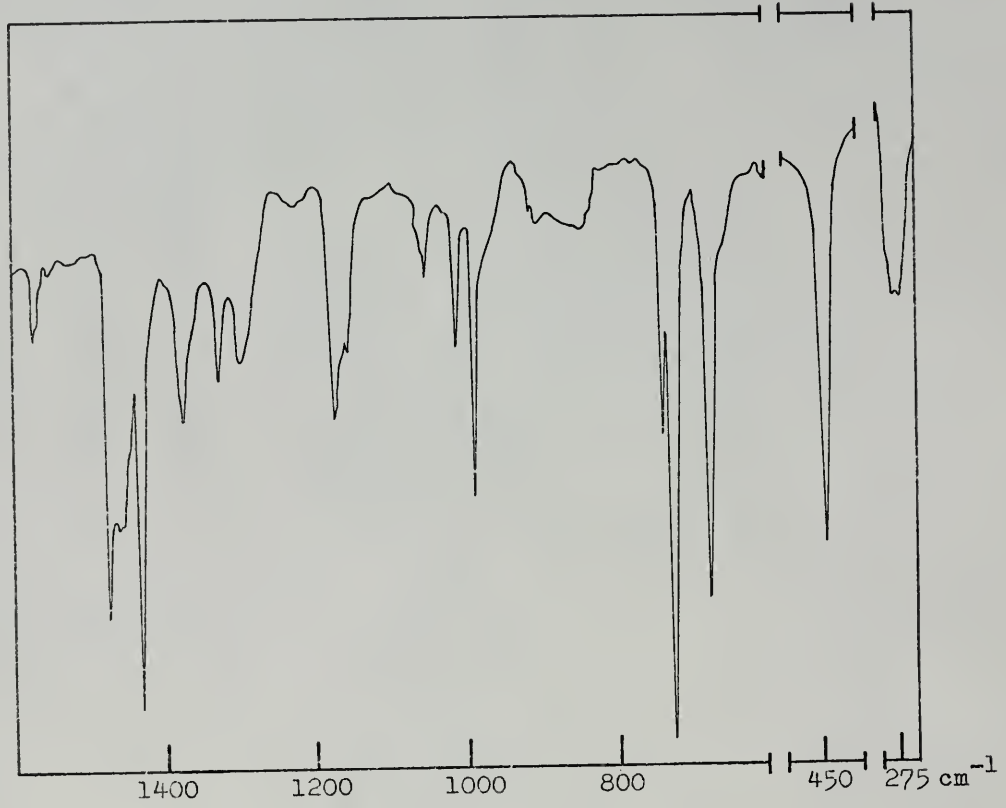


Fig. 20.-Infrared spectrum of $(C_6H_5)_3SbCl_2$.

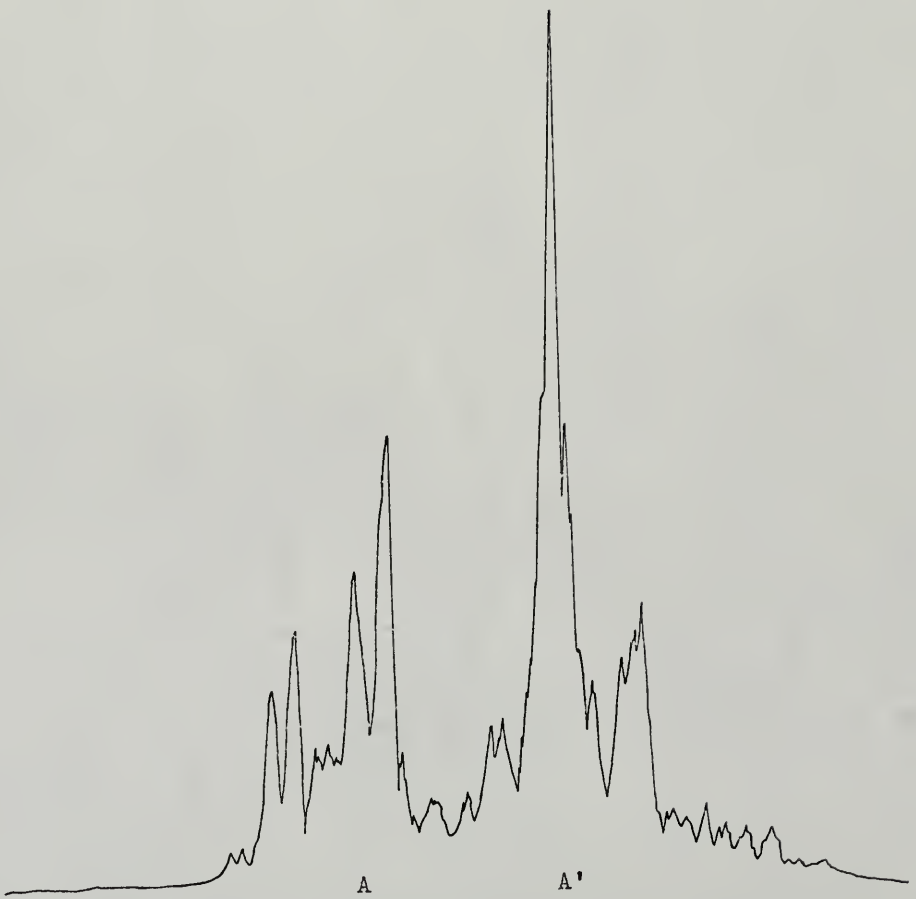


Fig. 21.-Proton magnetic resonance spectrum of $[(C_6H_5)_3Sb(Cl)]_2NH$.

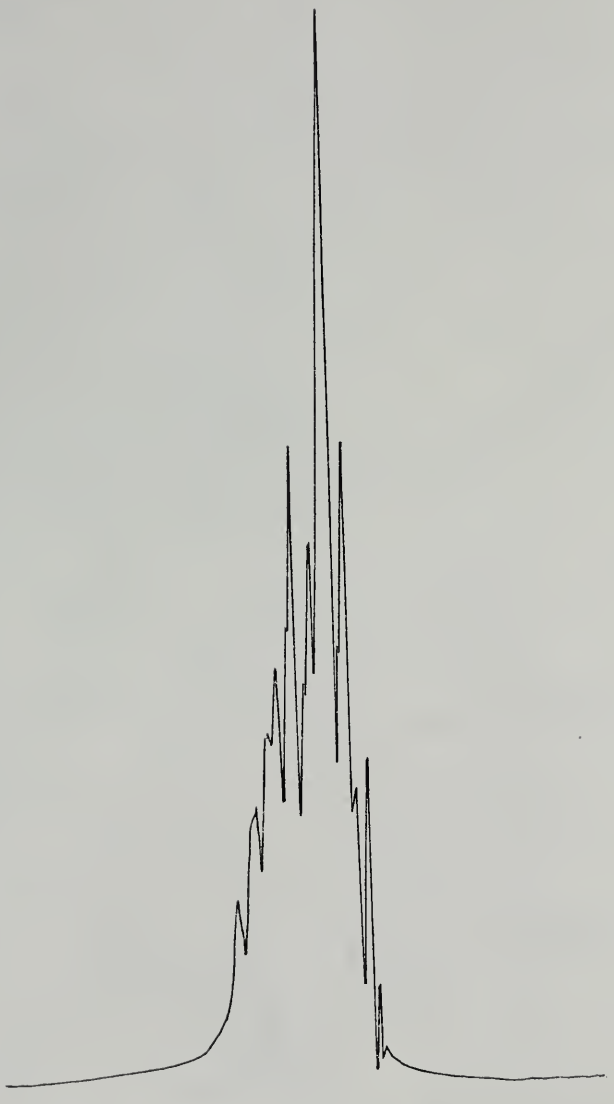


Fig. 22.-Proton magnetic resonance spectrum of $(C_6H_5)_3Sb$.

increasing height on the downfield side of the phenyl signal. When the spectrum was taken with respect to benzene it was found that the phenyl signal was almost symmetrically situated around the benzene signal.

Hydrolysis of the ammonia-free chloramination products

The alkyl chloramination products are readily hydrolyzed by exposure to moisture. Ammonia evolution is immediately noticeable. Dry iminobis-(triphenylchlorostibane) does not hydrolyze as readily as the alkyl derivatives. Hydrolysis probably occurs according to the following equation:

$$[R_3Sb(Cl)]_2NH + H_2O \rightarrow [R_3Sb(Cl)]_2O + NH_3$$

Oxybis-(trimethylchlorostibane)

$$[(CH_3)_3Sb(Cl)]_2NH + H_2O \rightarrow [(CH_3)_3Sb(Cl)]_2O + NH_3$$

Iminobis-(trimethylchlorostibane), 0.83 mmole, was ground and exposed to the atmosphere until ammonia evolution ceased. There was no noticeable weight change. The resulting compound decomposed at temperatures above 200°C. to a white solid and a volatile, highly reactive, liquid. The material can be recrystallized from alcohol. Large crystals of this compound tend to break up into powder at about 220°C. The yield was 100 per cent of theory based on the above equation (not recrystallized).

Oxybis-(trimethylchlorostibane) is soluble in water and hot alcohol and slightly soluble in chloroform. The infrared spectrum of oxybis-(trimethylchlorostibane) is shown in Figure 23 and has been discussed in a previous publication (13).

Anal. Calcd. for $[(CH_3)_3Sb(Cl)]_2O$: Cl, 16.85. Found: Cl, 16.66.

The proton magnetic resonance spectrum of oxybis-(trimethylchlorostibane) is shown in Figures 24 ($CDCl_3$) and 25 (H_2O). The spectrum in which chloroform was used as solvent is complex and probably results from a reaction between the compound and solvent. This apparently does not happen when water is used as a solvent, as a lone peak is observed which results from the methyl protons.

Oxybis-(triethylchlorostibane)

$$[(C_2H_5)_3Sb(Cl)]_2NH + H_2O \rightarrow [(C_2H_5)_3Sb(Cl)]_2O + NH_3$$

In a typical experiment, 1.23 mmoles of iminobis-(triethylchlorostibane) was dissolved in a methanol-water mixture and stirred for one hour. The solvent was removed by vacuum leaving an oil as residue. The oil was dissolved in boiling cyclohexane and upon cooling to room temperature white plate-like crystals formed. The yield was 0.62 gram which was 100 per cent of theory based on the above equation. The material melted at 179-180°C.

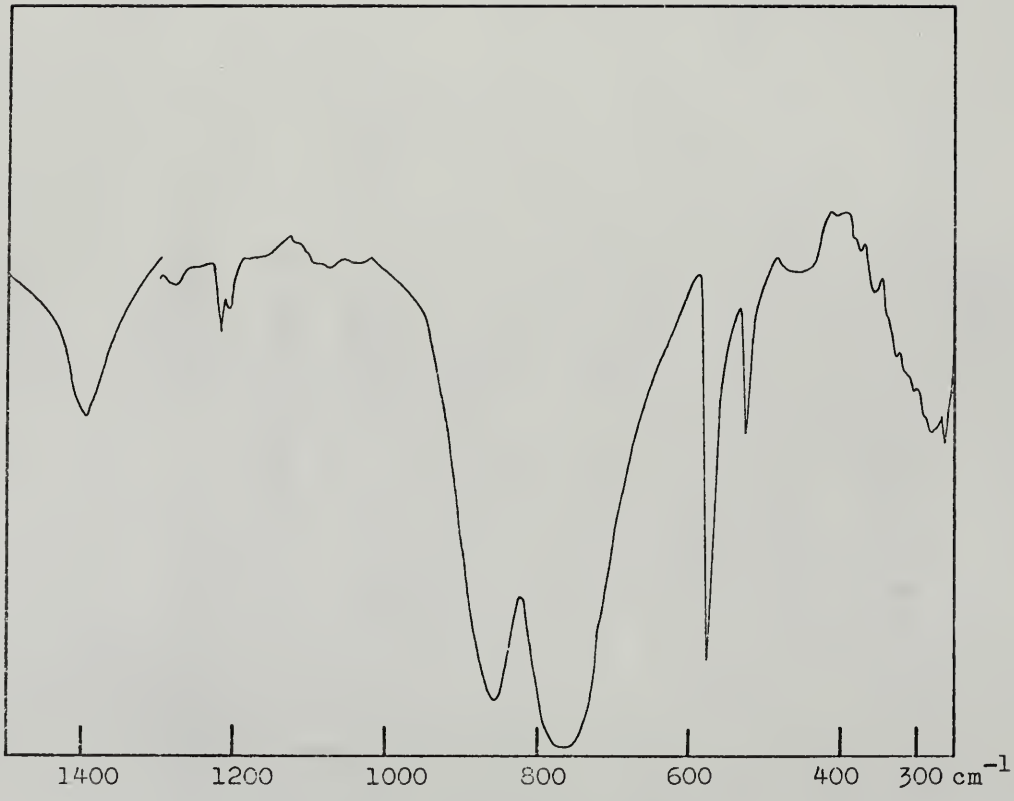


Fig. 23.-Infrared spectrum of $[(CH_3)_3Sb(Cl)]_2O$.

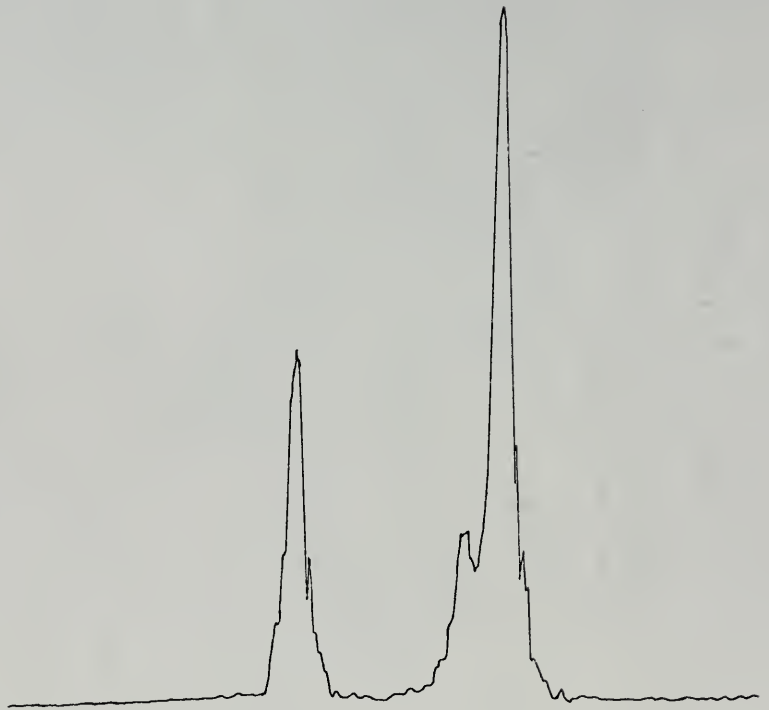


Fig. 24.-Proton magnetic resonance spectrum of $[(CH_3)_3Sb(Cl)]_2O$ ($CDCl_3$).

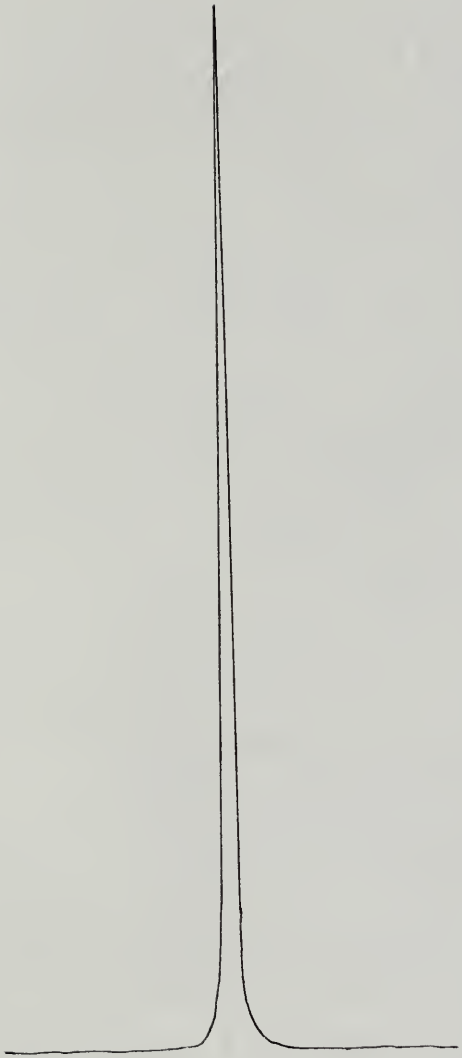


Fig. 25.-Proton magnetic resonance spectrum of $[(CH_3)_3Sb(Cl)]_2O$ (H_2O).

Oxybis-(triethylchlorostibane) is soluble in water, alcohol, benzene and hot cyclohexane and is insoluble in various ethers. It is hygroscopic, readily sublimes in vacuum, and decomposes when heated above its melting point at atmospheric pressure. The infrared spectrum is shown in Figure 26.

Anal. Calcd. for $[(C_2H_5)_3Sb(Cl)]_2O$: C, 28.54; H, 5.99; Cl, 14.04; MW, 505. Found: C, 28.92; H, 5.92; Cl, 14.18; MW, 497.

The proton magnetic resonance spectrum of oxybis-(triethylchlorostibane) is shown in Figure 27. Peak A results from the methylene protons and peak B from the methyl protons.

Oxybis-(tri-n-propylchlorostibane)

$$[(n\text{-}C_3H_7)_3Sb(Cl)]_2NH + H_2O \rightarrow [(n\text{-}C_3H_7)_3Sb(Cl)]_2O + NH_3$$

Iminobis-(tri-n-propylchlorostibane), 0.49 mmole, was exposed to the atmosphere and allowed to remain until ammonia evolution ceased. The solid was recrystallized from n-hexane. A total of 0.24 gram was obtained which was 84 per cent of theory based on the above equation. The compound melted at 98-100°C.

Oxybis-(tri-n-propylchlorostibane) is soluble in benzene, chloroform and hot n-hexane and is insoluble in water. An x-ray powder pattern was obtained using a sweep

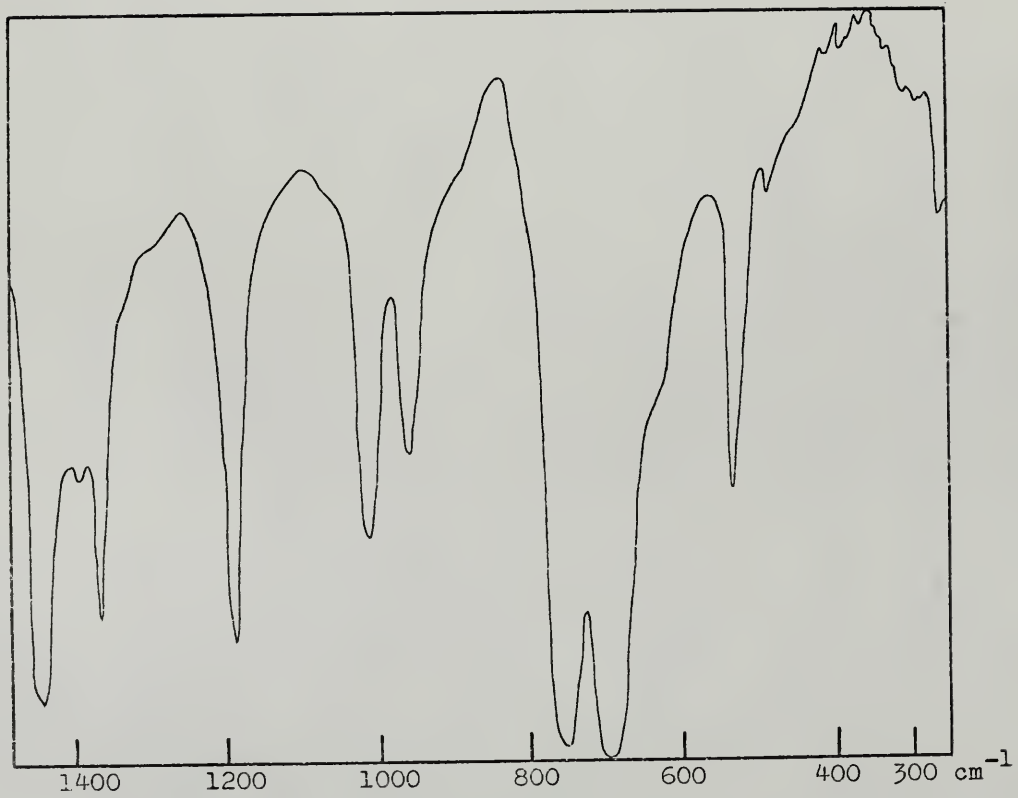


Fig. 26.-Infrared spectrum of $[(C_2H_5)_3Sb(Cl)]_2O$.

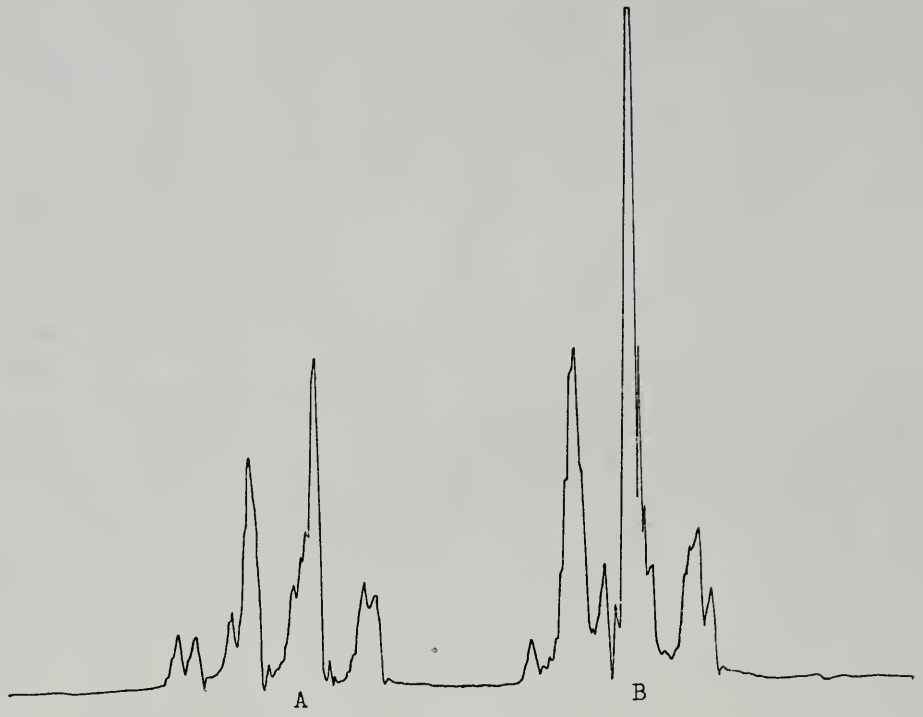


Fig. 27.-Proton magnetic resonance spectrum of $[(C_2H_5)_3Sb(Cl)]_2O$.

rate of one-fourth of a degree per minute. The angles and relative intensities are listed in Table 2. The relative intensities were calculated from measurements taken directly from the recorded spectrum.

TABLE 2

X-RAY POWDER DATA FOR $[(\underline{n}\text{-}C_3H_7)_3Sb(Cl)]_2O$

Angle, Θ	I	Angle, Θ	I
5.11	10.0	11.86	0.36
6.14	2.12	12.68	0.67
9.46	1.45	13.96	2.07
9.61	0.62	14.11	0.52
10.23	3.01	15.04	0.67
10.37	0.95	15.42	0.98
10.93	1.24	16.41	0.41
11.32	0.62	18.75	0.36
11.48	0.57	18.88	0.67

The infrared spectrum of oxybis-(tri-n-propylchlorostibane) is shown in Figure 28.

Anal. Calcd. for $[(\underline{n}\text{-}C_3H_7)_3Sb(Cl)]_2O$: C, 36.71; H, 7.19; Sb, 41.34; Cl, 12.04; MW, 589. Found: C, 36.75; H, 7.16; Sb, 41.39; Cl, 11.75; MW, 635.

The proton magnetic resonance spectrum of oxybis-(tri-n-propylchlorostibane) is shown in Figure 29. Peak A is attributed to the methylene protons and peak B to the methyl protons.

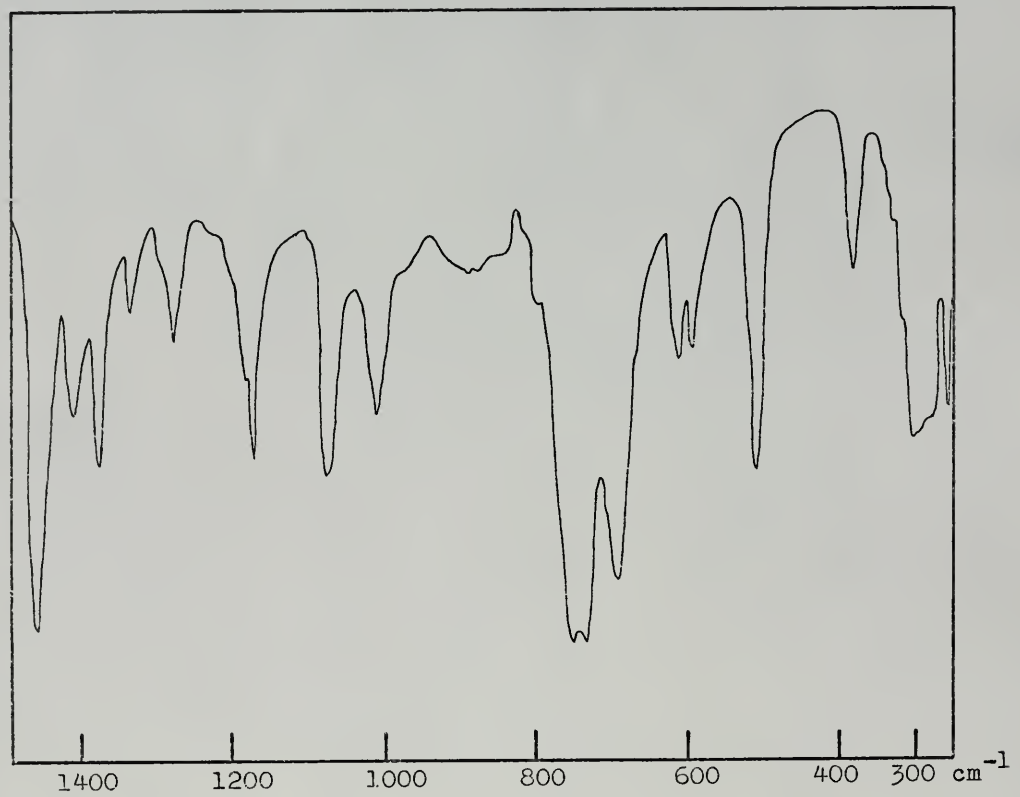


Fig. 28.-Infrared spectrum of $[(\underline{n}\text{-}C_3H_7)_3Sb(Cl)]_2O$.

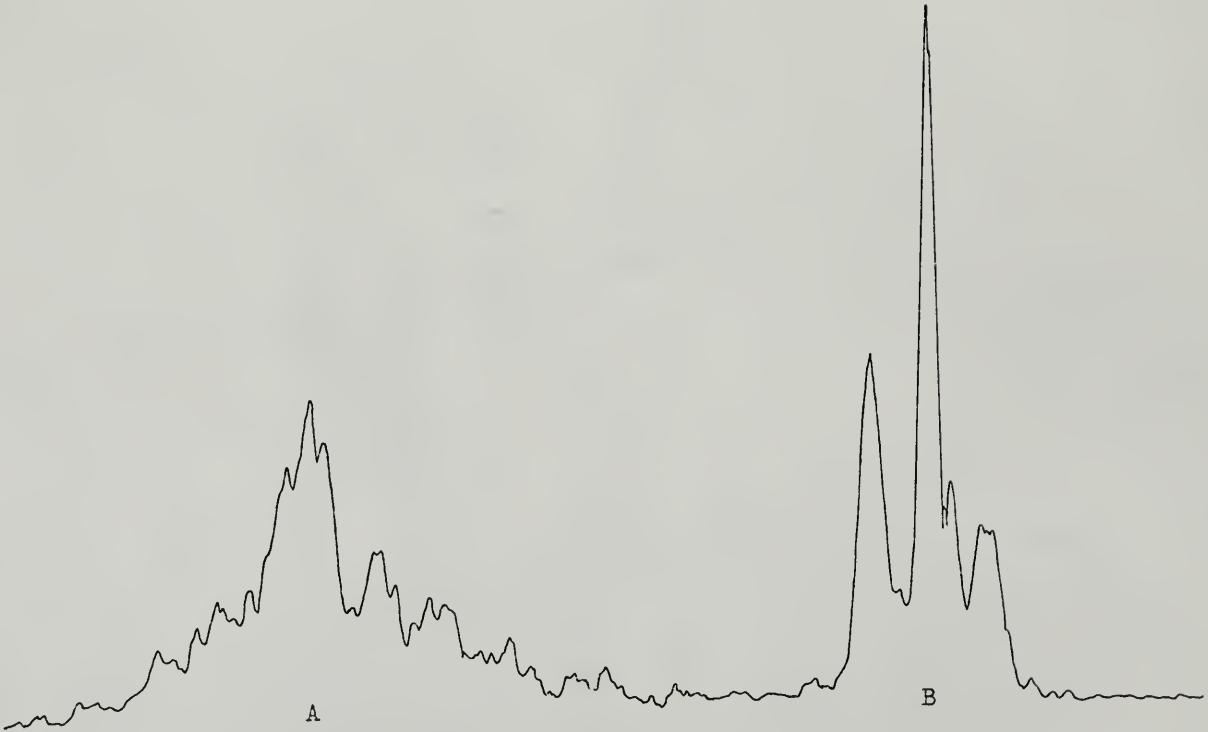


Fig. 29.-Proton magnetic resonance spectrum of $[(\underline{n}\text{-}C_3H_7)_3Sb(Cl)]_2O$.

Oxybis-(tri-n-butylchlorostibane)

$$[(n\text{-}C_4H_9)_3Sb(Cl)]_2NH + H_2O \rightarrow [(n\text{-}C_4H_9)_3Sb(Cl)]_2O + NH_3$$

Iminobis-(tri-n-butylchlorostibane), 0.28 mmole, was exposed to the atmosphere until ammonia evolution was complete. The product was compressed between porous plates until a flaky white solid was obtained with a melting point of 52-54°C. The yield was 0.16 gram which was 85 per cent of theory based on the above equation.

Oxybis-(tri-n-butylchlorostibane) is soluble in most common organic solvents and water. The infrared spectrum of this compound is shown in Figure 30.

Anal. Calcd. for $[(n\text{-}C_4H_9)_3Sb(Cl)]_2O$: C, 42.83; H, 8.09; Cl, 10.54. Found: C, 43.03; H, 8.11; Cl, 10.60.

The proton magnetic resonance spectrum was not obtained for this compound.

Oxybis-(triphenylchlorostibane)

$$[(C_6H_5)_3Sb(Cl)]_2NH + H_2O \rightarrow [(C_6H_5)_3Sb(Cl)]_2O + NH_3$$

Iminobis-(triphenylchlorostibane), 0.56 mmole, was suspended in wet acetone and warmed until ammonia evolution ceased. The solvent was removed by vacuum and the residual white solid was recrystallized from benzene to yield 0.42 gram of a solid which melted at 219-222°C. [Lit. (12) m.p. 222°C.]. A mixed melting point determination with an authentic sample of oxybis-(triphenylchlorostibane) showed

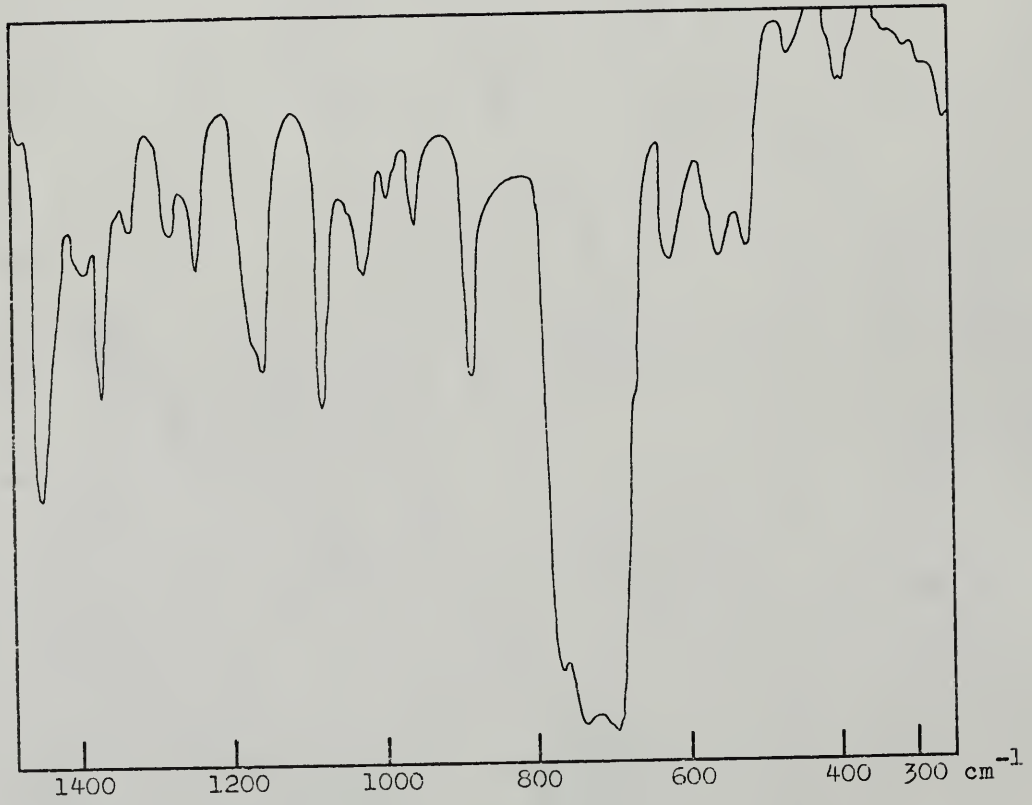


Fig. 30.-Infrared spectrum of $[(\underline{n}\text{-}C_4H_9)_3Sb(Cl)]_2O$.

no depression and the solid did not release ammonia when treated with base. The infrared spectrum is shown in Figure 31.

Analytical data were not obtained.

Figure 32 shows the proton magnetic resonance spectrum of oxybis-(triphenylchlorostibane). Peak A is assigned to the ortho protons of the phenyl groups and peak A' to the meta and para protons of the phenyl groups. The spectrum was taken using benzene as an internal standard and it was found that the ortho proton signal was shifted -21.2 cps from the benzene signal. The meta and para proton signal was not shifted significantly from that of benzene.

Some reactions of organoantimony(V) compounds

A variety of miscellaneous reactions of some organoantimony(V) compounds were carried out in order to obtain products from which infrared and proton magnetic resonance data could be obtained. In most cases yield data were not obtained.

Pyrolysis of oxybis-(trimethylchlorostibane)

$$3[(CH_3)_3Sb(Cl)]_2O \xrightarrow{\Delta} Sb_2O_3 + 4(CH_3)_3Sb + 6CH_3Cl$$

Oxybis-(trimethylchlorostibane), 2.02 mmoles, was placed in a small flask equipped with a take-off head and receiver. The apparatus was thoroughly evacuated and then

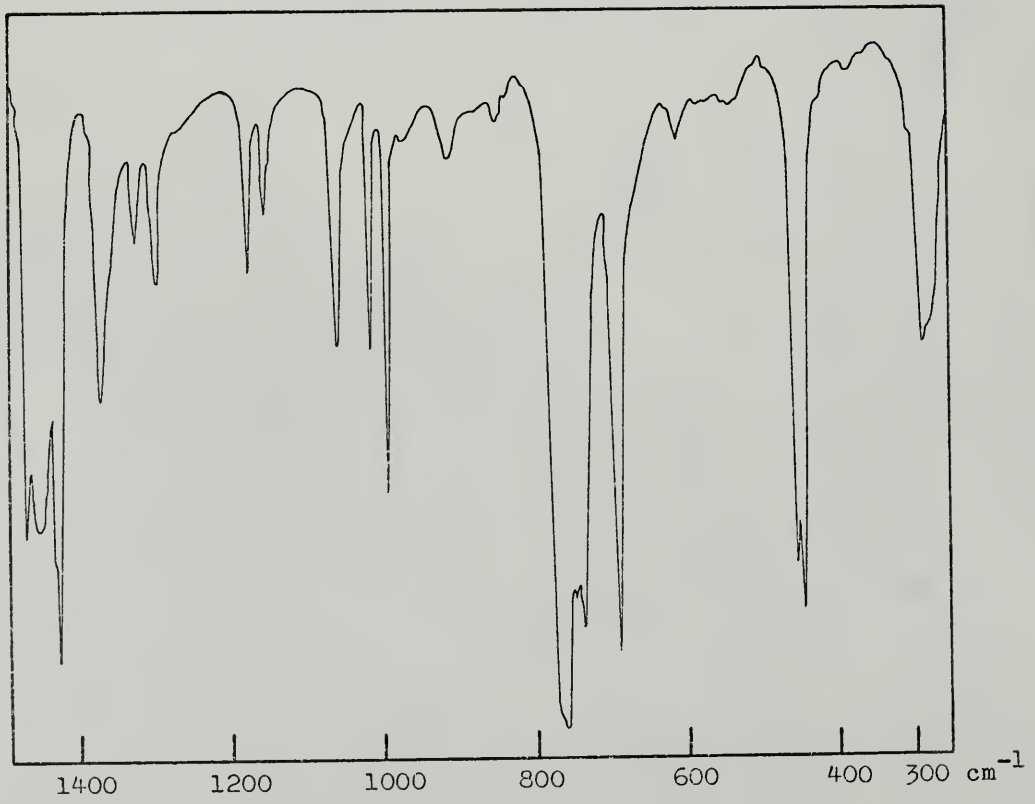


Fig. 31.-Infrared spectrum of $[(C_6H_5)_3Sb(Cl)]_2O$.

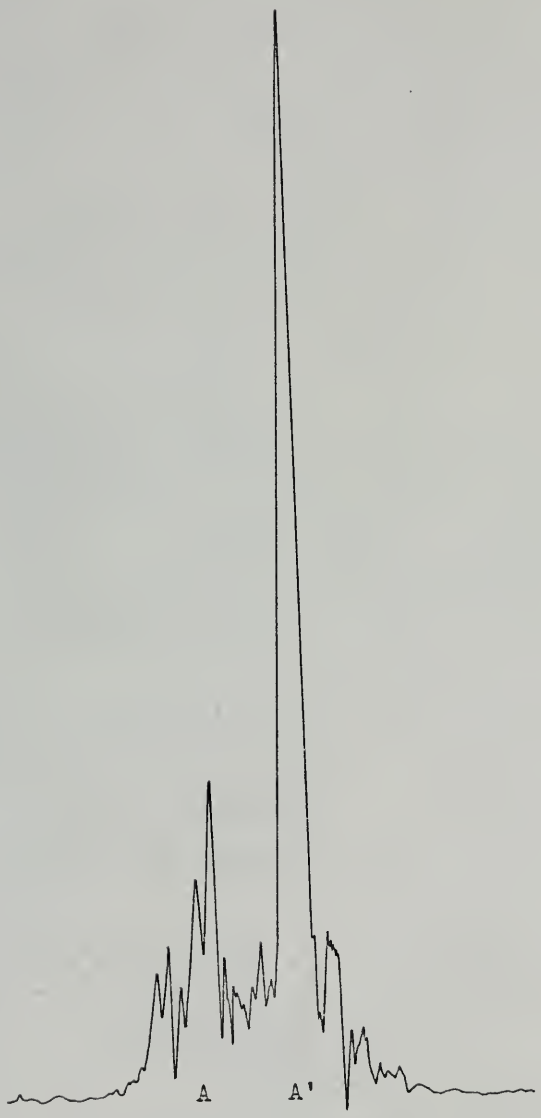


Fig. 32.-Proton magnetic resonance spectrum of $[(C_6H_5)_3Sn(Cl)]_2O$.

brought to atmospheric pressure with dry nitrogen. The flask was slowly heated until a maximum temperature of 260°C. was reached and held for one half hour. During this time a liquid distilled and was identified as trimethylstibine by vapor pressure measurements (21). A total of 0.32 gram was obtained which was 71.4 per cent of theory.

The solid residue was identified as antimony(III) oxide by comparison of its infrared spectrum with that of an authentic sample of the compound (22). The residue weighed 0.18 gram which was 92.6 per cent of theory based on the above equation. Methyl chloride was assumed to be the other product, but was not measured in this experiment.

The infrared spectrum of antimony(III) oxide is shown in Figure 33.

Trimethyldichlorostibane

$$[(CH_3)_3Sb(Cl)]_2O + 2HCl_{(conc.)} \rightarrow 2(CH_3)_3SbCl_2 + H_2O$$

An aqueous solution of oxybis-(trimethylchlorostibane), 1.31 mmole, was treated with an excess of concentrated hydrochloric acid. A white compound, insoluble in water, was formed and was recrystallized from the acidic reaction solvent. The yield was 0.49 gram (79 per cent of theory based on the above equation). The material melted at 230-230.5°C. (dec.) [Lit. (17) m.p. 229-230°C. (dec.)].

Trimethyldichlorostibane is soluble in chloroform, boiling water and boiling toluene. The infrared spectrum of

Fig. 33.-Infrared spectrum of Sb_2O_3.

trimethyldichlorostibane is shown in Figure 34 and is consistent with that found in the literature (13).

Anal. Calcd. for $(CH_3)_3SbCl_2$: Cl, 29.8. Found: Cl, 29.8.

The proton magnetic resonance spectrum of trimethyldichlorostibane is shown in Figure 35. The single peak results from the methyl protons. This spectrum is entirely consistent with the established crystal structure of the molecule (23), which is trigonal bipyramidal with the methyl groups in the equatorial positions.

Oxybis-(trimethylnitratostibane)

$$[(CH_3)_3Sb(Cl)]_2O + 2Ag^+ + 2NO_3^- \rightarrow [(CH_3)_3Sb(ONO_2)]_2O + 2AgCl$$

Aqueous silver nitrate was added dropwise to an aqueous solution of oxybis-(trimethylchlorostibane) until precipitation was complete. The resulting silver chloride was removed by filtration and the solution was evaporated to dryness. The residual white solid was recrystallized from alcohol to yield a material that melted at 262°C. (dec.). No yield data were obtained since the compound was prepared for the purpose of obtaining infrared and proton magnetic resonance spectra.

Oxybis-(trimethylnitratostibane) is soluble in water and slightly soluble in chloroform. The infrared spectrum of this compound is shown in Figure 36. The very strong,

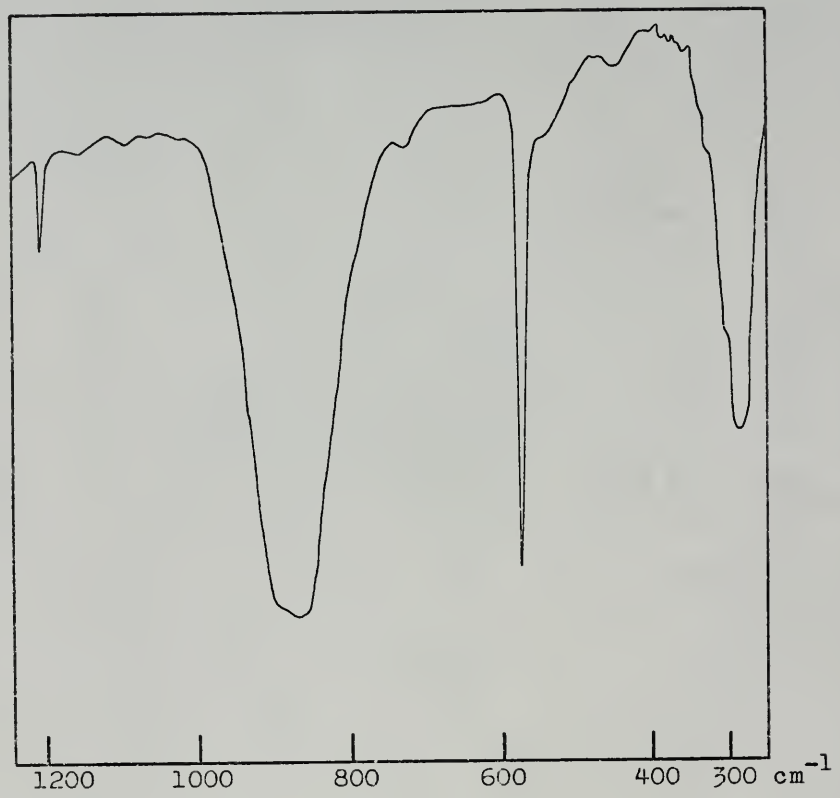


Fig. 34.-Infrared spectrum of $(CH_3)_3SbCl_2$.

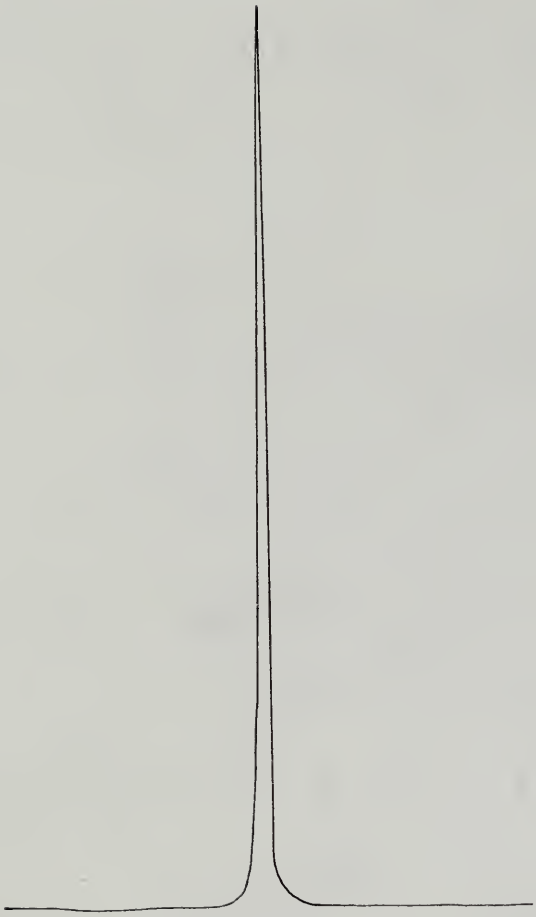


Fig. 35.-Proton magnetic resonance spectrum of $(CH_3)_3SbCl_2$.

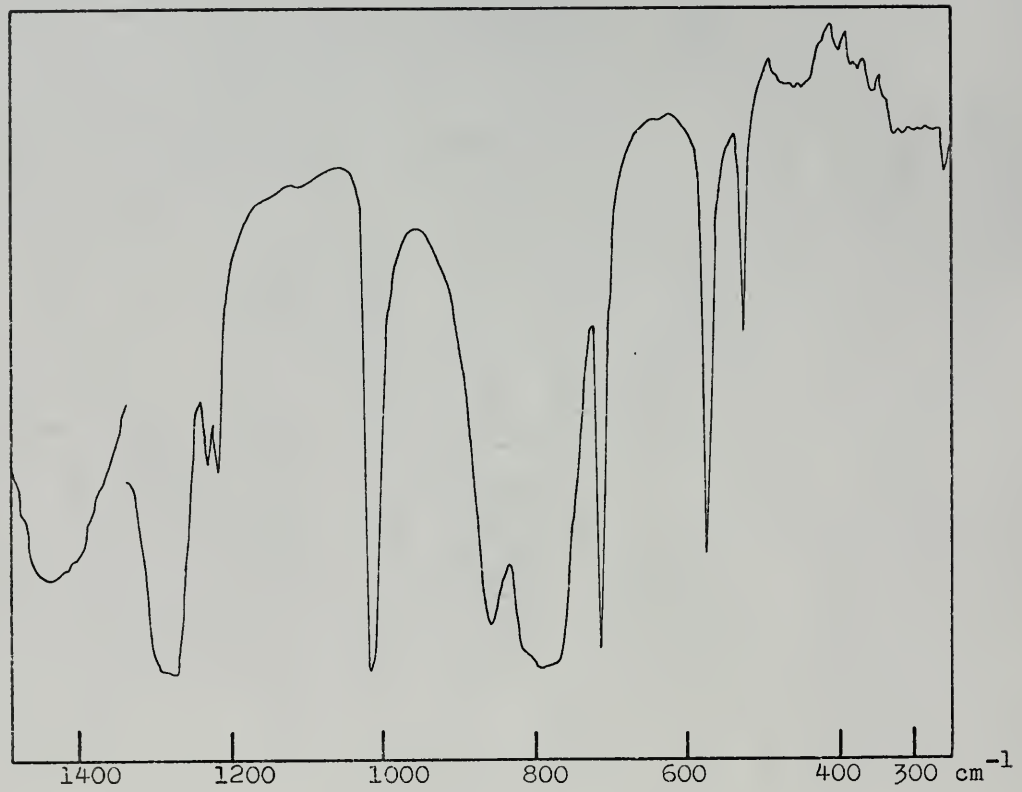


Fig. 36.-Infrared spectrum of $[(CH_3)_3Sb(ONO_2)]_2O$.

broad, peaks at 1480-1380 cm^{-1} and 1310-1275 cm^{-1} are attributed to the ν_4 and ν_1 absorption frequencies of the partially covalent nitrate group (24), which exhibits C_{2v} symmetry. It has been suggested that the degree of splitting between ν_4 and ν_1 is a measure of covalent character (25) as long as it exceeds 125 cm^{-1} (26). Any splitting less than this value might result from lattice distortion. Oxybis-(trimethylnitratostibane) has a $\nu_4 - \nu_1$ splitting of 137 cm^{-1}. Also, a strong absorption occurs at 1018 cm^{-1} which is the ν_2 mode for the covalent nitrato group. The ν_6 mode which usually occurs in the 800-781 cm^{-1} region is probably overlapped by the strong Sb-O-Sb absorption at 788 cm^{-1}.

Anal. Calcd. for $[(CH_3)_3Sb(ONO_2)]_2O$: C, 15.21; H, 3.83; N, 5.91. Found: C, 15.20; H, 3.90; N, 5.98.

The proton magnetic resonance spectrum of oxybis-(trimethylnitratostibane) is shown in Figure 37. The single peak results from the methyl protons. When chloroform was used as the solvent, three peaks resulted as was the case with iminobis- and oxybis-(trimethylchlorostibanes).

Trimethyldinitratostibane

$$(CH_3)_3SbBr_2 + 2Ag^+ + 2NO_3^- \rightarrow (CH_3)_3Sb(ONO_2)_2 + 2AgBr$$

Trimethyldinitratostibane was prepared by the method of Long et al. (13) in which an aqueous solution of trimethyldibromostibane was reacted with aqueous silver nitrate

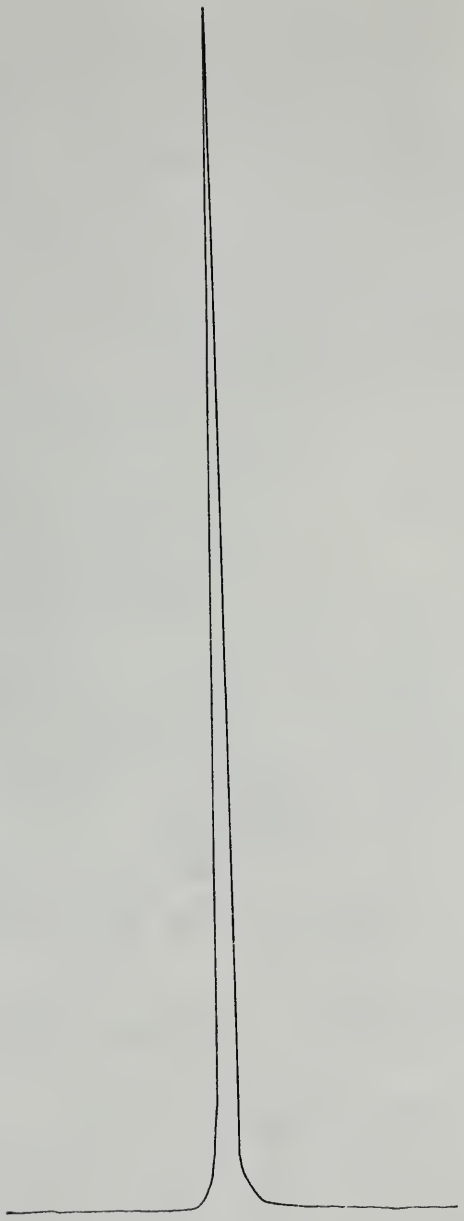


Fig. 37.-Proton magnetic resonance spectrum of $[(CH_3)_3Sb(ONO_2)]_2O$.

until the precipitation of silver bromide was complete. The solution was freed of silver bromide by filtration and the water was removed by vacuum. The residual solid was recrystallized from alcohol. The resulting crystals melted at 149-150°C. No yield data were obtained.

Trimethyldinitratostibane is soluble in water and chloroform. The infrared spectrum is shown in Figure 38. The $\nu_4 - \nu_1$ splitting is 240 cm^{-1}. The spectrum of this compound was discussed by Long (13) and later by Clark and Goel (27). Our work agrees quite closely with that of the latter authors although no special reaction conditions were maintained.

Anal. Calcd. for $(CH_3)_3Sb(ONO_2)_2$: C, 12.39; H, 3.12; N, 9.63. Found: C, 12.25; H, 3.22; N, 9.44.

The proton magnetic resonance spectrum of trimethyldinitratostibane is shown in Figure 39. The lone peak results from the methyl protons.

Oxybis-(triethylnitratostibane)

$$[(C_2H_5)_3Sb(Cl)]_2O + 2Ag^+ + 2NO_3^- \rightarrow [(C_2H_5)_3Sb(ONO_2)]_2O + 2AgCl$$

An aqueous solution of oxybis-(triethylchlorostibane) was reacted with an aqueous solution of silver nitrate until precipitation was complete. The solution was filtered free of silver chloride and evaporated to dryness by vacuum. The

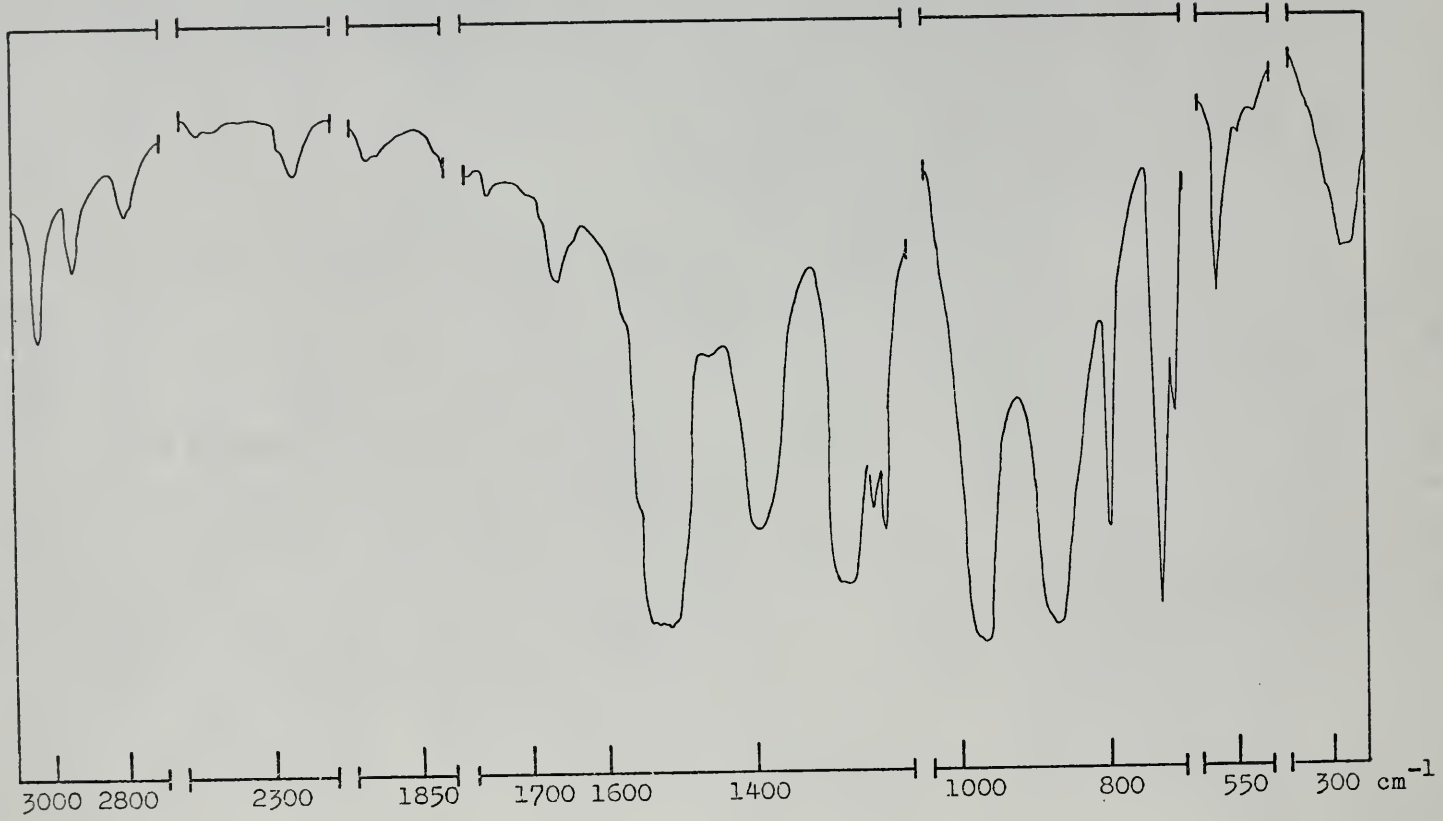


Fig. 38.-Infrared spectrum of $(CH_3)_3Sb(ONO_2)_2$.

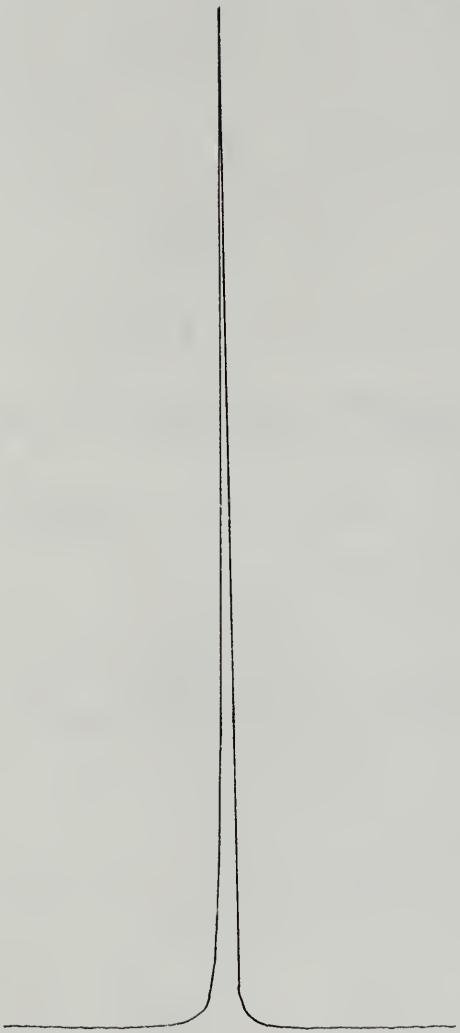


Fig. 39.-Proton magnetic resonance spectrum of $(CH_3)_3Sb(ONO_2)_2$.

resulting compound melted with decomposition at 233°C. after recrystallization from alcohol. No yield data were obtained.

The infrared spectrum of oxybis-(triethylnitratostibane) is shown in Figure 40. The $\nu_4 - \nu_1$ splitting is 165 cm^{-1}. Some of the other characteristic absorptions are partially or completely overlapped by C-H absorptions and are therefore not observed or occur as shoulders.

Anal. Calcd. for $[(C_2H_5)_3Sb(ONO_2)]_2O$: C, 25.83; H, 5.42. Found: C, 26.45; H, 5.78.

Proton magnetic resonance data were not obtained for this compound.

Tri-n-butyldichlorostibane (28,29,30)

$$3(n\text{-}C_4H_9)_3Sb + 2SbCl_3 \rightarrow 3(n\text{-}C_4H_9)_3SbCl_2 + 2Sb$$

Resublimed antimony(III) chloride, 0.137 mole, was dissolved in 100 milliliters of dry benzene and slowly added to tri-n-butylstibine, 0.204 mole, with vigorous stirring in a dry nitrogen atmosphere. The colorless liquid clouded and turned yellow, then orange, then brown, and finally black. The mixture was stirred overnight and then heated to 50°C. for two hours. During this time the black solid turned metallic gray. The liquid was filtered in a dry box and the benzene was removed under reduced pressure. The higher boiling liquid residue was distilled under vacuum. A total of 61.8 grams of a liquid that boiled at 120-125°C. at

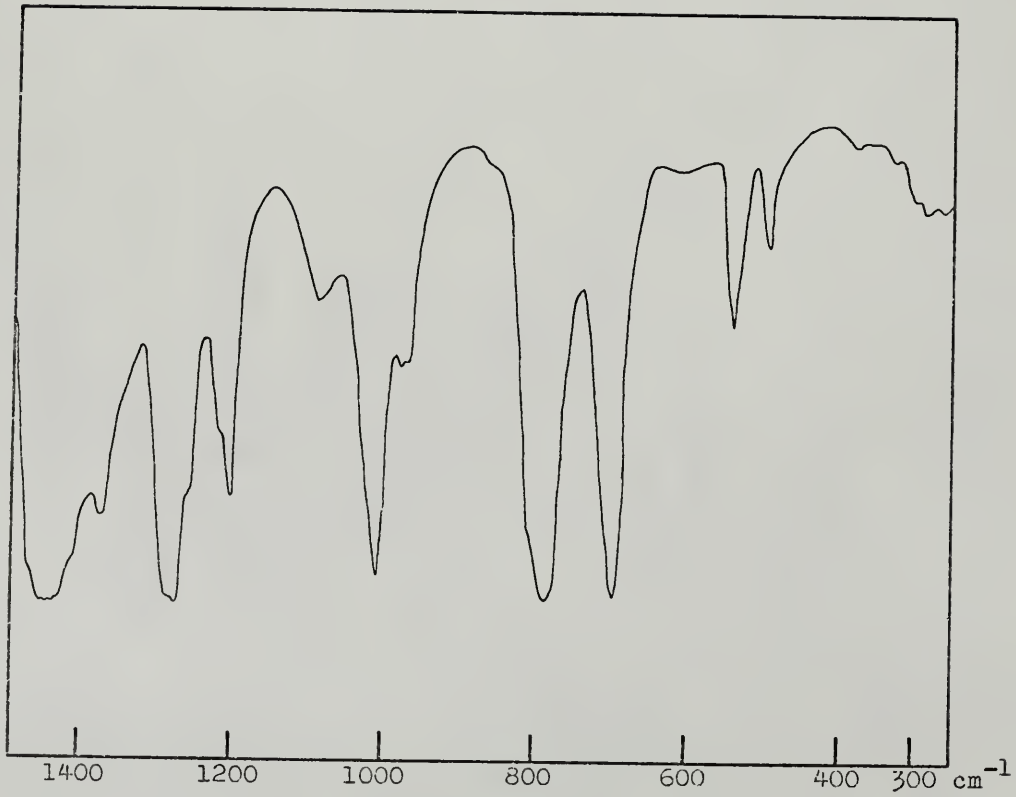


Fig. 40.-Infrared spectrum of $[(C_2H_5)_3Sb(ONO_2)]_2O$.

0.14 mm was collected (83 per cent of theory based on the above equation).

Tri-n-butyldichlorostibane is a colorless, mobile, liquid which slowly hydrolyzes when exposed to the atmosphere. It decomposes to an orange, high-boiling liquid and a low-boiling liquid when heated over 200°C. at 200 mm pressure. The orange liquid boils at 121-123°C. at 10 mm. Since compounds of the type R_2SbX are commonly prepared by heating the corresponding R_3SbX_2 (9,18) it is probable that the orange liquid is di-n-butylchlorostibine. No analytical data were obtained since the orange compound partially decomposed upon standing with the deposition of a black solid. The yield was 89 per cent of theory. The infrared spectra of tri-n-butyldichlorostibane and di-n-butylchlorostibine are shown in Figures 41 and 42, respectively.

Anal. Calcd. for $(n\text{-}C_4H_9)_3SbCl_2$: C, 39.59; H, 7.48; Cl, 19.48. Found: C, 39.59; H, 7.36; Cl, 19.32.

Proton magnetic resonance data were not obtained for either of the two compounds.

Triphenyldichlorostibane

$$[(C_6H_5)_3Sb(Cl)]_2O + 2HCl_{(g)} \xrightleftharpoons[\text{excess } H_2O]{\text{excess HCl}} 2(C_6H_5)_3SbCl_2 + H_2O$$

A hot benzene solution of oxybis-(triphenylchlorostibane), 3.85 mmoles, was treated with excess gaseous

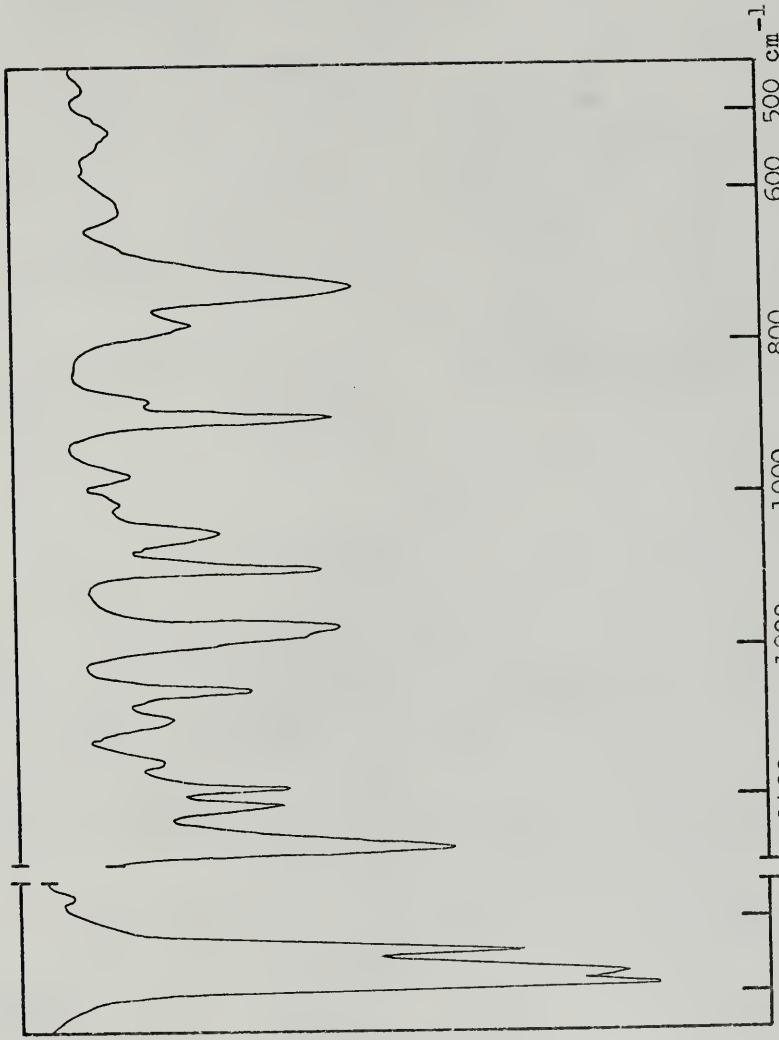


Fig. 41.--Infrared spectrum of $(n\text{-}C_4H_9)_3SbCl_2$.

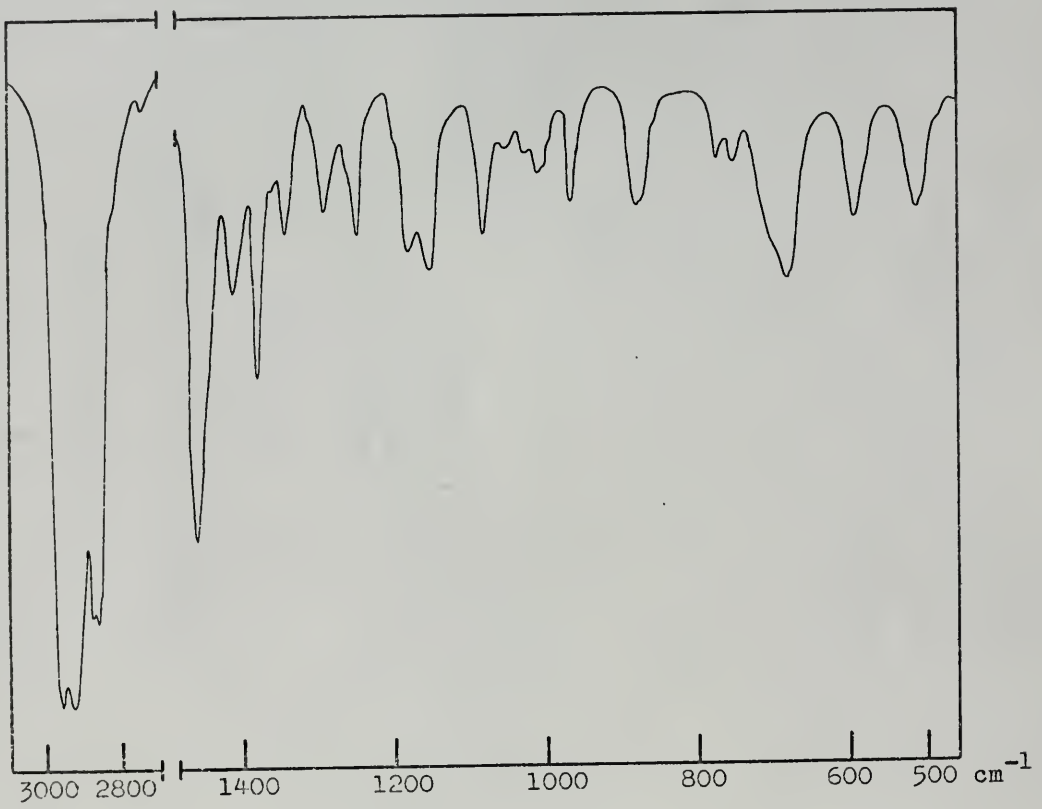


Fig. 42.-Infrared spectrum of ($\underline{n}$-$C_4H_9)_2SbCl$.

hydrogen chloride and then allowed to cool to room temperature. No crystals appeared at this point indicating that reaction was complete. About 10 milliliters of alcohol was added, the solution was heated to boiling, and the benzene was removed by passing nitrogen directly through the hot liquid. White needles were obtained by recrystallization from the alcohol. A total of 2.86 grams of the crystalline product was obtained which was 87.6 per cent of theory based on the above equation. The solid melted at 143-144°C. and showed no depression in the melting point when mixed with an authentic sample of triphenyldichlorostibane.

Triphenyldichlorostibane is soluble in benzene, hot ethyl acetate and hot alcohol and slightly soluble in ether, n-hexane, cyclohexane and carbon tetrachloride. The infrared spectrum is shown in Figure 20.

Elementary analyses were not required.

The proton magnetic resonance spectrum of triphenyldichlorostibane is shown in Figure 43. The peak labelled A is assigned to the ortho protons of the phenyl groups and peak A' to the meta and para protons. The area ratio of A to A' is approximately 2 to 3 as would be expected. The spectrum was also taken with respect to internal benzene and it was found that the ortho proton pattern was shifted -55.5 cps from the benzene signal and the meta and para proton pattern was shifted -8.5 cps. This gives some

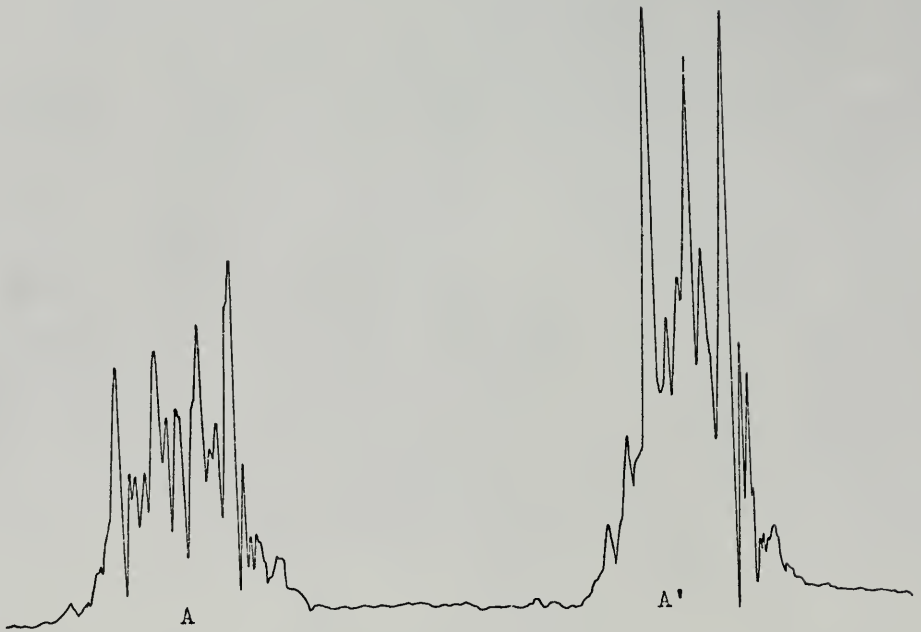


Fig. 43.-Proton magnetic resonance spectrum of $(C_6H_5)_3SbCl_2$.

insight into the electron withdrawing ability of the Cl-Sb-Cl group and is in complete agreement with the results of an x-ray study of this compound (31). It was found that the crystal structure of triphenyldichlorostibane is trigonal bipyramidal with the phenyl groups in the equatorial plane and the chlorine atoms in the axial positions. The Sb-Cl bond length appears to be somewhat larger than normal thereby placing a large delta positive charge on antimony and explaining why the Cl-Sb-Cl group functions as a good electrophile. It is almost comparable to a nitro group, which shifts the ortho proton signal -56.9 cps from the benzene signal (32).

Triphenylstibine oxide (33)

$$(C_6H_5)_3SbCl_2 + 2OH^- \rightarrow (C_6H_5)_3SbO + H_2O + 2Cl^-$$

An alcoholic solution of triphenyldichlorostibane was added to a boiling aqueous solution of sodium hydroxide. A white solid formed immediately. The liquid was boiled for an additional 30 minutes and then the solid was filtered free of liquid. The insoluble solid was washed with cold water until the wash water was neutral and chloride free. The compound was dried by vacuum and found to melt at 235-290°C. with decomposition. Since the material was prepared for the purpose of performing an infrared study, no yield data were obtained.

Anal. Calcd. for $(C_6H_5)_3SbO$: C, 58.57; H, 4.10. Found: C, 58.70; H, 4.28.

Triphenylstibine oxide appears to be relatively insoluble in most common organic solvents. Figure 44 shows the infrared spectrum of this compound. The peak at 660 cm^{-1} is attributed to the polymeric Sb-O-Sb absorption.

Attempts to prepare triphenylstibine oxide from triphenyldichlorostibane by treatment with refluxing water and vigorous stirring for several days (34) yielded only oxybis-(triphenylchlorostibane).

The proton magnetic resonance spectrum of triphenylstibine oxide was not obtained.

Triphenylstibine oxide hydrate

$$(C_6H_5)_3SbO + xH_2O \rightarrow (C_6H_5)_3SbO \cdot xH_2O$$

Triphenylstibine oxide was treated with boiling, moist, benzene until a portion of the solid dissolved. The benzene was filtered free of solid and allowed to slowly cool thereby producing a white solid. The recrystallized solid melted at 209-212°C.

The infrared spectrum of triphenylstibine oxide partial hydrate is shown in Figure 45. The absorption at 655 cm^{-1} is attributed to the polymeric Sb-O-Sb vibration.

Anal. Calcd. for $(C_6H_5)_3SbO \cdot 0.3H_2O$: C, 57.79; H, 4.19. Found: C, 57.79; H, 4.20.

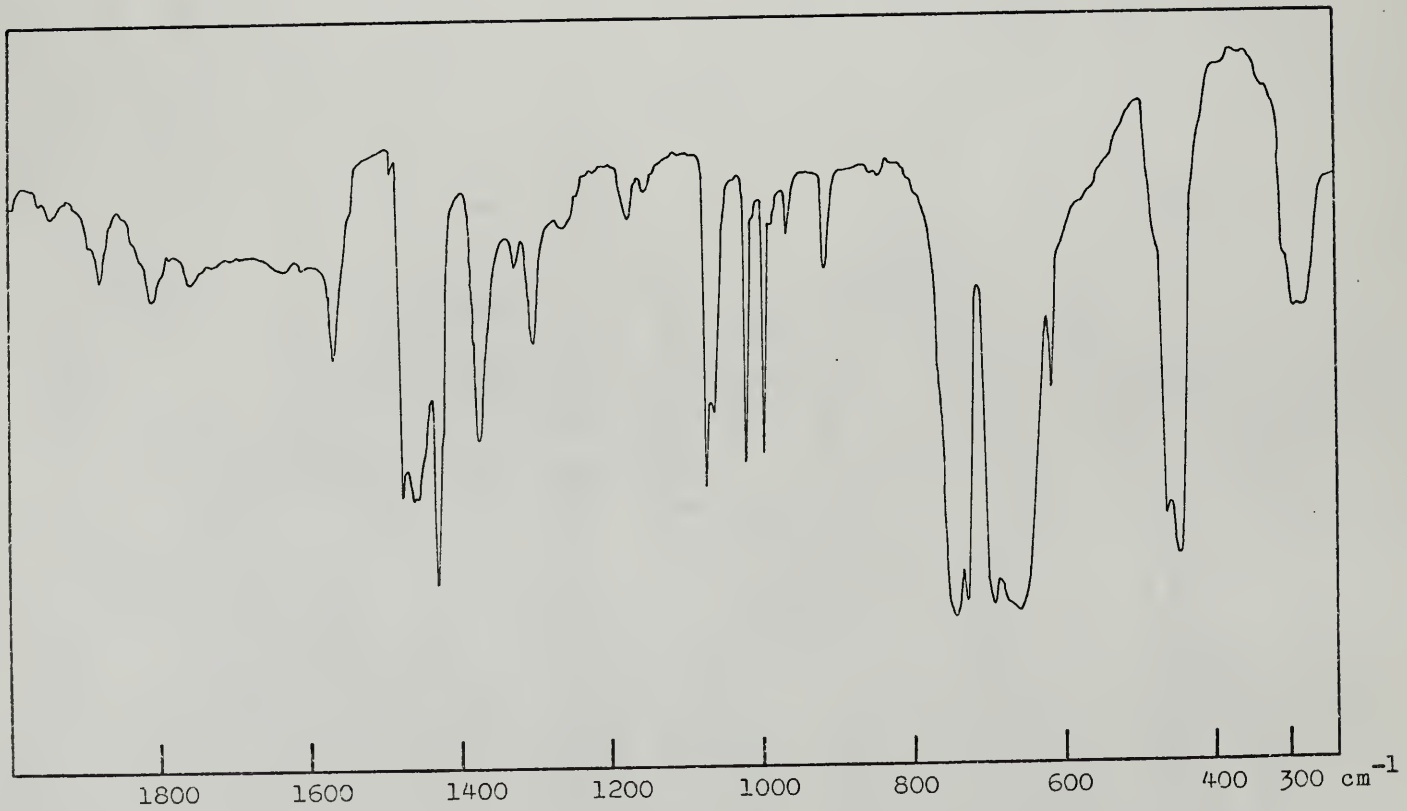


Fig. 44.-Infrared spectrum of $(C_6H_5)_3SbO$.

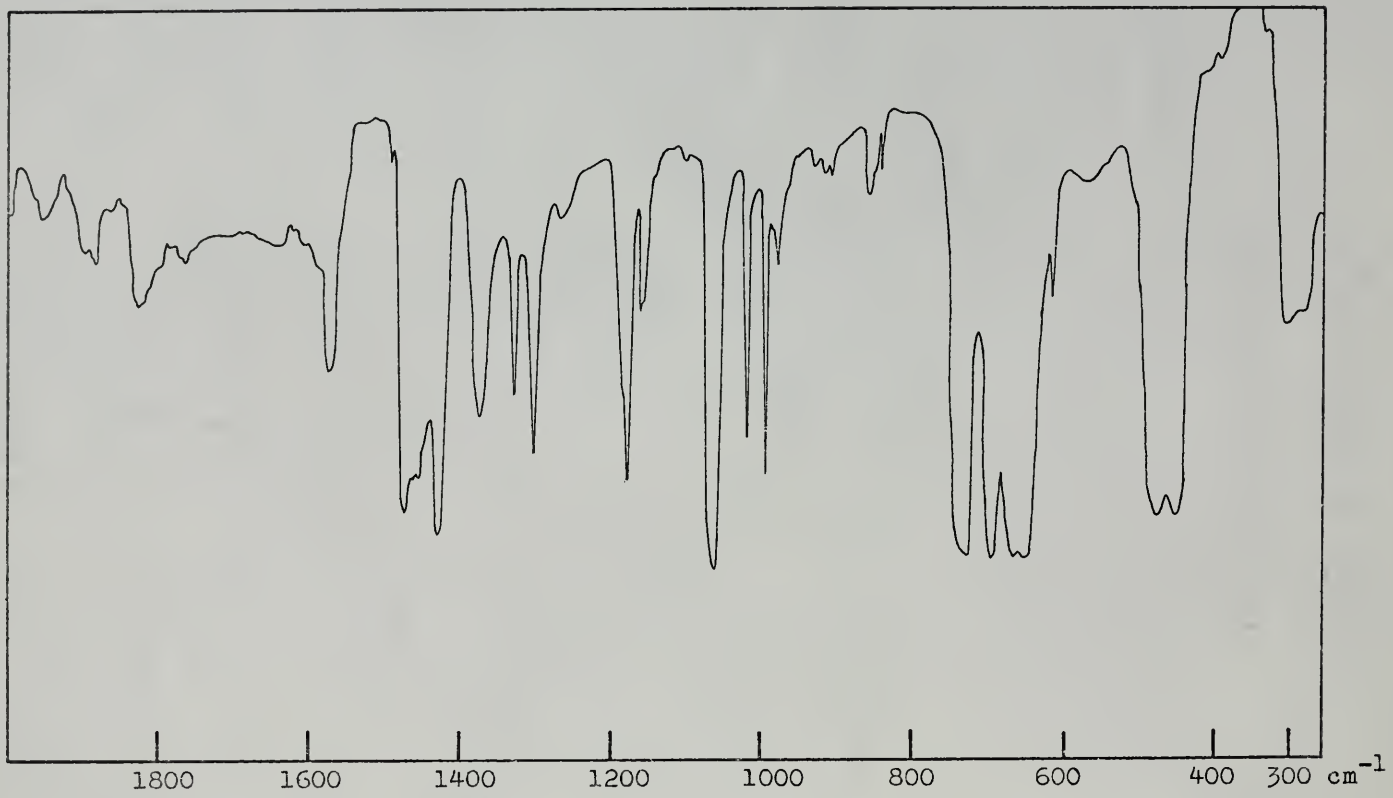


Fig. 45.-Infrared spectrum of $(C_6H_5)_3SbO \cdot 0.3H_2O$.

Figure 46 shows the proton magnetic resonance spectrum of triphenylstibine oxide partial hydrate. The peak labelled A is assigned to the ortho protons of the phenyl groups and peak A' to the meta and para protons. The area ratio of A to A' is approximately 2 to 3. The ortho protons are shifted -27 cps from the benzene signal while the meta and para proton pattern fall symmetrically around the benzene signal. The signal for the protons attached to oxygen was not observed and is presumed to be overlapped by the phenyl signal or not resolved from the background.

Oxybis-(triphenylnitratostibane)

$$2(C_6H_5)_3SbCl_2 + 4AgNO_3 + H_2O \xrightarrow[2.H_2O]{1.alc.} [(C_6H_5)_3Sb(ONO_2)]_2O + 4AgCl + 2HNO_3$$

Oxybis-(triphenylnitratostibane) was prepared by the method of Morgan et al. (8), in which an alcoholic solution of triphenyldichlorostibane was treated with an alcoholic solution of silver nitrate. The resulting white solid was recrystallized from water and found to melt at 226°C. (dec.). No yield data were obtained.

Figure 47 shows the infrared spectrum of oxybis-(triphenylnitratostibane). All the characteristic covalent nitrato-group absorptions are present and the $\nu_4 - \nu_1$ splitting is 220 cm^{-1}. The Sb-O-Sb absorption has apparently been shifted to a lower wave number such that it is now

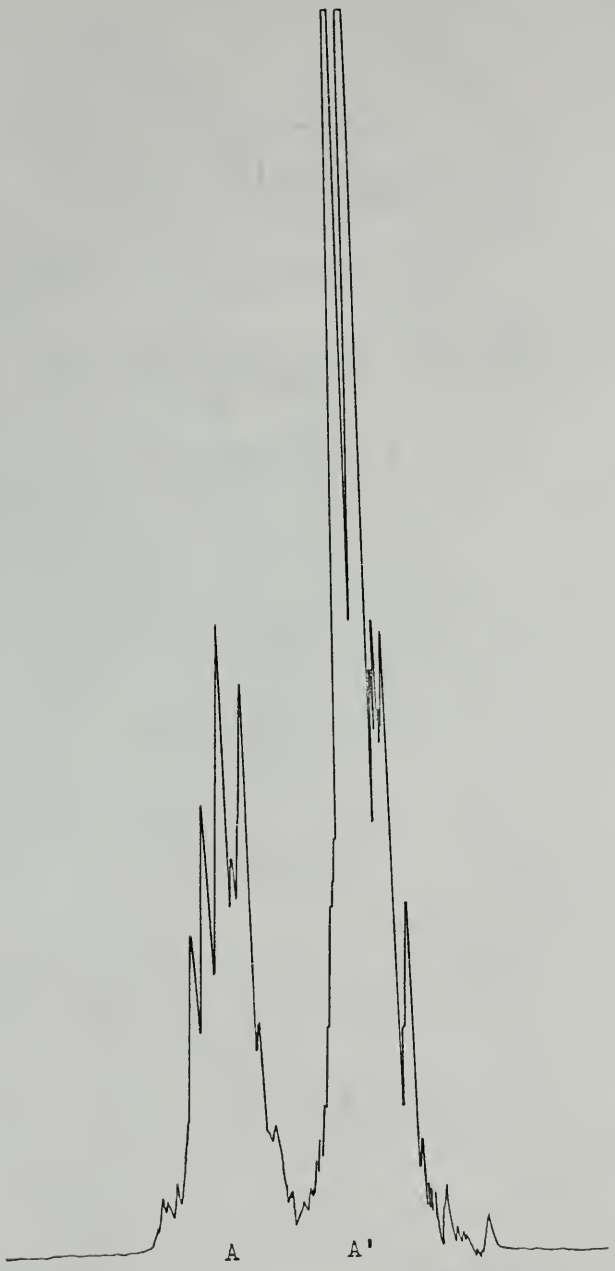


Fig. 46.-Proton magnetic resonance spectrum of $(C_6H_5)_3SbO \cdot 0.3H_2O$.

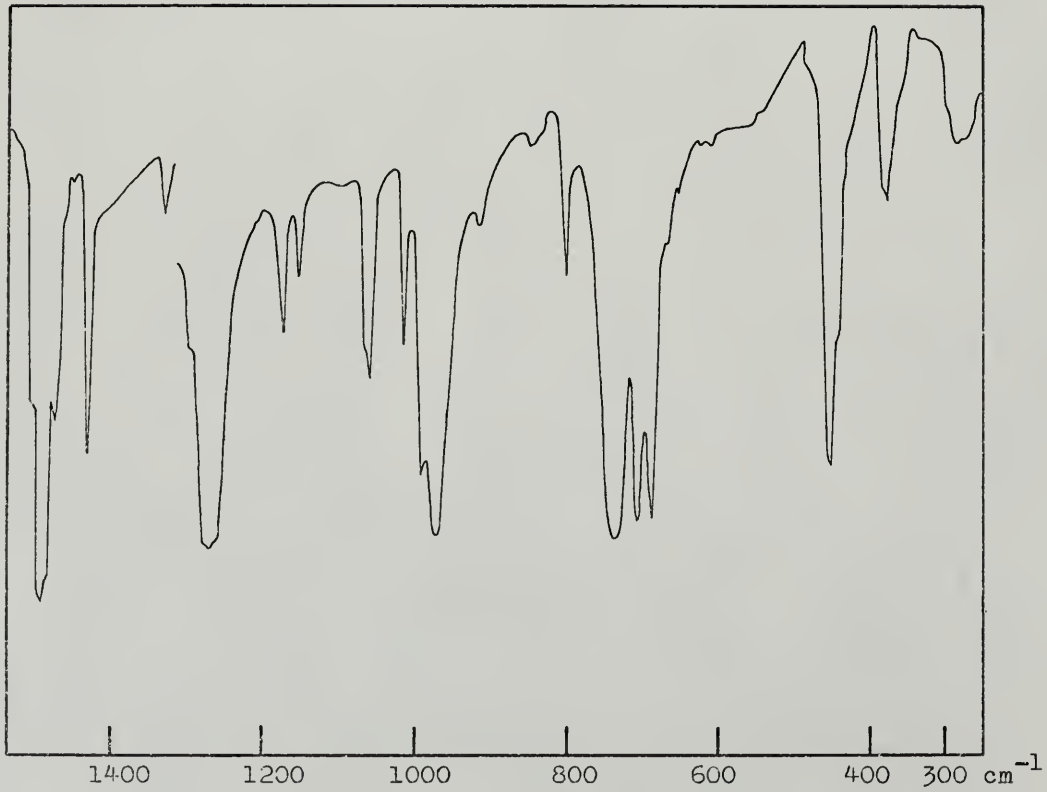


Fig. 47.-Infrared spectrum of $[(C_6H_5)_3Sb(ONO_2)]_2O$.

overlapped by the characteristic phenyl absorption in the 740 cm^{-1} region.

Anal. Calcd. for $[(C_6H_5)_3Sb(ONO_2)]_2O$: C, 51.10; H, 3.57; N, 3.31. Found: C, 51.00; H, 3.64; N, 3.31.

The proton magnetic resonance spectrum of oxybis-(triphenylnitratostibane) is shown in Figure 48. The phenyl absorption is shown as a rather complex signal in which the chemical shift values for the ortho, meta, and para protons are similar. The chemical shift from the benzene signal was not measured.

Discussion

The main purpose of this study was to investigate the reaction of chloramine with various trialkylstibines and triphenylstibine. The results clearly establish the generality of the chloramine-tertiary stibine reaction and also shows, at least in part, that chloramine reacts with stibines in a manner analogous to its reaction with amines, phosphines and arsines. Another fact brought out by this work is that rigorously anhydrous conditions must be maintained at all times as the resulting antimony-nitrogen compounds rapidly hydrolyze.

The trimethylstibine-ammonia-free chloramine reaction proceeds quite vigorously at room temperature producing

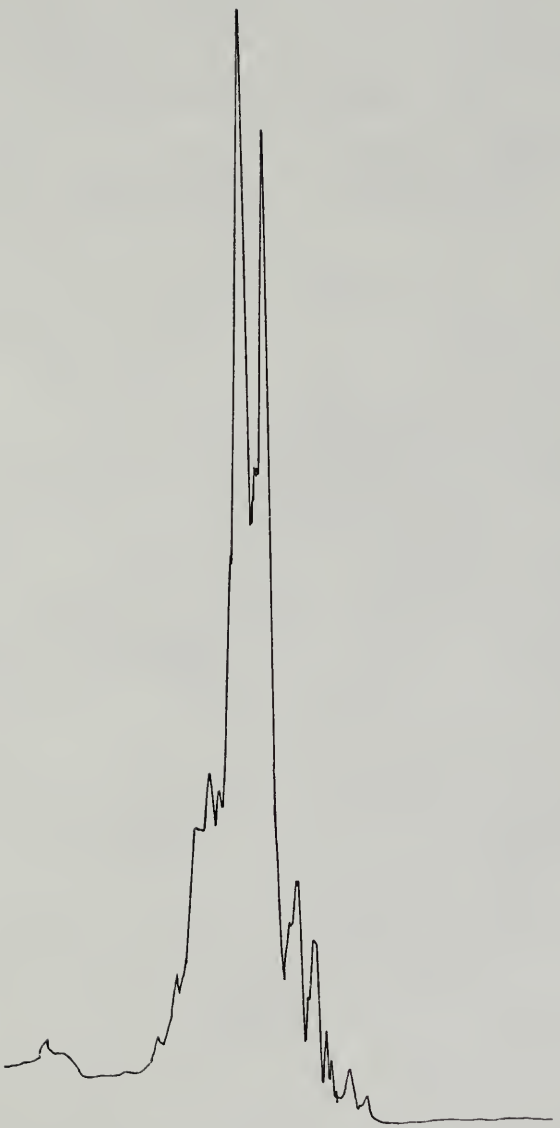


Fig. 48.-Proton magnetic resonance spectrum of $[(C_6H_5)_3Sb(ONO_2)]_2O$.

iminobis-(trimethylchlorostibane) in good yield together with what appears to be a few percent of trimethyldichlorostibane. The reaction is postulated to proceed according to the following equations:

$$\text{I} \quad (CH_3)_3Sb_{(soln)} + NH_2Cl_{(soln)} \rightarrow (CH_3)_3Sb(NH_2)Cl_{(s)}$$

$$\text{II} \quad 2(CH_3)_3Sb(NH_2)Cl_{(s)} \rightarrow [(CH_3)_3Sb(Cl)]_2NH_{(s)} + NH_{3(g)}$$

The product of step I has never been isolated and there is no evidence available to verify its existence for any length of time, but to postulate it as an intermediate is quite logical since compounds of this type are the principal products of the reaction of chloramine with tertiary amines, tertiary phosphines, and tertiary arsines. In the latter cases, however, the compounds are salt-like, whereas in the case at hand, the compound is thought to be molecular. Since the above reaction proceeds even at temperatures as low as -78°C., it was first suspected that the amino compound was the product at low temperature and then as the material was allowed to warm to room temperature step II became the predominant reaction.

Both the amino and the imino compounds should act as bases towards anhydrous gaseous hydrogen chloride thereby producing a mixture of trimethyldichlorostibane and ammonium chloride. The Sb:N:Cl ratio for the mixture might enable one to show which compound had actually reacted with the hydrogen chloride. The reaction would probably proceed

according to the following equations for:

(1) aminotrimethylchlorostibane,

$$(CH_3)_3Sb(NH_2)Cl_{(s)} + 2HCl_{(g)} \rightarrow (CH_3)_3SbCl_{2(s)} + NH_4Cl_{(s)}$$

Sb:N:Cl = 1:1:3

(2) iminobis-(trimethylchlorostibane),

$$[(CH_3)_3Sb(Cl)]_2NH_{(s)} + 3HCl_{(g)} \rightarrow 2(CH_3)_3SbCl_{2(s)} + NH_4Cl_{(s)}$$

Sb:N:Cl = 2:1:5

Trimethylstibine was allowed to react with chloramine at temperatures between -78° and -45°C. producing a thermally unstable solid which was allowed to react immediately with gaseous hydrogen chloride. The Sb:N:Cl ratio obtained for the mixture was 1.9:1.0:5.1 thereby indicating that even at these low temperatures the imino compound, or more accurately, a species giving an Sb:N:Cl ratio of 2:1:5, was present and not aminotrimethylchlorostibane.

The few percent of trimethyldichlorostibane formed in the reaction is one of the more uncommon cases whereby chloramine functions as a chlorinating agent. The formation of this product is postulated to proceed according to one of the following equations:

$$(CH_3)_3Sb(NH_2)Cl_{(s)} + NH_2Cl_{(soln)} \rightarrow (CH_3)_3SbCl_{2(s)} + 1/3N_{2(g)} + 4/3NH_{3(g)}$$

or

$$2(CH_3)_3Sb(NH_2)Cl_{(s)} \rightarrow (CH_3)_3SbCl_{2(s)} + (CH_3)_3Sb_{(soln)} + 1/3N_{2(g)} + 4/3NH_{3(g)}$$

The similarity between the above chlorination and that of tri-n-butylstibine by antimony(III) chloride is quite noticeable and it is probable that the reaction mechanisms are also similar.

During the past few years some work (13,14,23,35,36, 37) concerning infrared data on antimony(V) compounds has appeared in the literature. Various vibrational assignments have been made, with probably the most interesting being the assignment for the Sb-O-Sb linkage and the Sb-C symmetrical stretching vibration. The infrared spectrum of iminobis-(trimethylchlorostibane) shows all the characteristic absorptions which result from the methyl groups, but more particularly, it shows a very strong peak at 741 cm^{-1} and a weak peak at 533 cm^{-1}. One would expect the Sb-NH-Sb linkage to give rise to an infrared absorption in the same general region as that resulting from the Sb-O-Sb linkage and it is for this reason that the 741 cm^{-1} absorption is assigned to the Sb-NH-Sb asymmetrical stretching vibration. The weak band at 533 cm^{-1} might result from an Sb-N vibration, but one cannot rule out the possibility that it might also result from the Sb-C symmetrical stretching mode. Normally this latter mode is infrared inactive, but a lowering of symmetry could render the vibration infrared active. The $\geq$N-H stretching vibration appears as a medium peak at 3225 cm^{-1}. No $\geq$N-H deformation mode is found in the

spectrum. This latter piece of data indicates that the material is truly an imino compound, since the $\geq$N-H deformation absorption is very weak and normally not observed in solid state spectra. The increased absorption which occurs just under 300 cm^{-1} might result from the Sb-Cl stretching vibration, but no definite assignment can be made without further data from the far infrared region.

The proton magnetic resonance data for this compound are inconclusive. Solubility limitations and extreme sensitivity of the compound to hydrolysis limited the choice of solvents to chloroform. This proved to be a highly unfavorable solvent since complex formation with this compound occurred. As a result, the proton magnetic resonance spectrum showed three rather complex peaks instead of the expected single peak which would have resulted from a compound containing equivalent methyl groups.

Chloramine acts only as an aminating agent when it reacts with triethyl-, tri-n-propyl-, and tri-n-butylstibines. The postulated reaction sequence is shown by the following equations:

$$\text{I} \quad R_3Sb + NH_2Cl \rightarrow R_3Sb(NH_2)Cl$$

$$\text{II} \quad 2R_3Sb(NH_2)Cl \rightarrow [R_3Sb(Cl)]_2NH + NH_3$$

Excellent yields are obtained for all three stibines when completely anhydrous ammonia-free chloramine is used and the reaction is carried out on a vacuum line. It is not

that ammonia-free chloramine is essential for the production of the iminobis-(trialkylchlorostibanes), for this compound is also formed with the ammonia-chloramine mixture from the gas phase generator (20). However, the process by which ammonia is removed is also an excellent method for removal of water, and vacuum line technique used in the reaction with ammonia-free chloramine assures that water will not be reintroduced into the system. In this manner the hydrolysis reaction is eliminated and a relatively pure product is obtained from the reaction. Since the imino compounds in question are difficult to recrystallize because of their tendencies to undergo decomposition, the production of essentially pure compounds is highly desirable.

The infrared spectra of the three new imino compounds, $[(C_2H_5)_3Sb(Cl)]_2NH$, $[(\underline{n}\text{-}C_3H_7)_3Sb(Cl)]_2NH$, and $[(\underline{n}\text{-}C_4H_9)_3Sb(Cl)]_2NH$, become increasingly more complicated as the alkyl group is lengthened. This is to be expected since more C-H and C-C stretching and deformation modes become possible as the size of the alkyl groups is increased. The infrared band assigned to the Sb-NH-Sb vibration appears at 758 cm^{-1} for iminobis-(triethylchlorostibane), at 752 cm^{-1} for iminobis-(tri-n-propylchlorostibane), and at either 768 cm^{-1} or 736 cm^{-1} for iminobis-(tri-n-butylchlorostibane). A band which might result from the Sb-C symmetrical stretching vibration appears in the ethyl analogue but apparently

is so weak in the other two cases that it is not resolved from the background. All three compounds show the typical $\geq$N-H absorption in the 3160 cm^{-1} region and all fail to show a deformation band. This again is more evidence in support of the proposed structure, $[R_3Sb(Cl)]_2NH$. Increased absorption occurs in the 250-300 cm^{-1} region, however, nothing definite can be said about this area except that it is the region where one would expect the Sb-Cl absorption to occur.

Molecular weight data were obtained for iminobis-(triethyl- and tri-n-butylchlorostibanes) and in both cases the results were about 18 per cent lower than that expected for the condensed materials. The molecular weight experiment was performed in a standard apparatus with some modification to help prevent hydrolysis, but nevertheless, hydrolysis did occur causing low values to be obtained.

The proton magnetic resonance spectra of the compounds failed to show an absorption which could be attributed to the imino proton. This is not unusual as in many cases an imino proton band is very weak and broad and difficult to resolve from the background. The part of the spectrum which results from the protons of the alkyl groups is entirely characteristic of the particular group in question and consistent with the proposed structure.

Triphenylstibine reacts with chloramine in the same manner as trimethylstibine in that triphenyldichlorostibane is a reaction product along with iminobis-(triphenylchlorostibane). There is no evidence of reaction until just under room temperature at which time a solid precipitates, the solvent takes on a light yellow color, and nitrogen is evolved. The experiment was carried out using different mole ratios and different concentrations of starting materials in order to determine the most favorable conditions for the formation of only the imino compound. The unpredictability of the ethereal chloramine solutions caused complications which prevented the study from yielding any definite information concerning the chlorinating reaction. However, upon compilation of data, it appeared that the production of triphenyldichlorostibane was dependent more upon a concentration effect than upon a mole ratio effect. To say more would be purely speculation without any chemical evidence to back it up. A mechanistic study of this type would require a unique set-up in which all variables could be controlled and still prevent the introduction of water and the decomposition of chloramine.

The infrared spectrum of iminobis-(triphenylchlorostibane) shows a weak absorption at 3140 cm^{-1} which is tentatively attributed to the $\geq$N-H stretching vibration. It should be pointed out that this peak is not resolved if

the compound is improperly mulled. The spectrum also shows the characteristic peaks associated with the phenyl groups. The very strong peaks at 1430 cm^{-1} and 995 cm^{-1}, which have in the past been associated with a P-phenyl linkage (38), are more properly assigned to an activated ring stretching vibration and a ring breathing mode, respectively (39). These peaks are found in essentially the same place in phosphorus, arsenic, antimony and bismuth compounds containing phenyl groups and it is unlikely that the peaks would always fall in the same place if they were actually metal-phenyl vibrations. The Sb-NH-Sb absorption occurs as a very strong band at 765 cm^{-1} and does not appreciably change when the compound is hydrolyzed. The $C_{(ar)}$-Sb asymmetrical stretching vibration is undoubtedly overlapped by the phenyl out-of-plane ring bending by quadrants vibration in the 450 cm^{-1} region (35,40). Figure 49 shows a plot of the $C_{(ar)}$-M observed frequencies in wave numbers, where M is equal to P, As, Sb, and Bi, versus $1/\sqrt{\mu}$, where μ represents the reduced mass, and clearly verifies the preceding statement. The Sb-Cl stretching vibration, which should occur in the 250-300 cm^{-1} region, either occurs below 250 cm^{-1} or is masked by the medium band at 285 cm^{-1}. This latter band is characteristic of Sb(V) compounds containing phenyl groups and probably results from infrared active bending modes associated with the (C_6H_5)-Sb-(C_6H_5) structure which is common to all of the phenyl compounds (14).

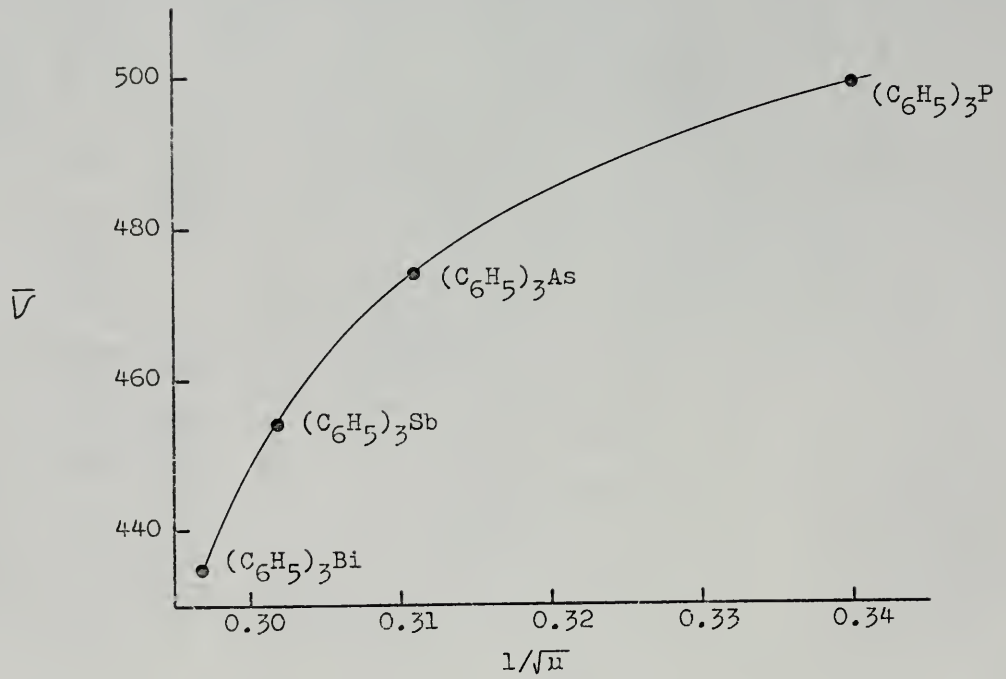


Fig. 49.--Plot of $C_{(ar)}$-Sb frequency versus $1/\sqrt{\mu}$.

The proton magnetic resonance spectrum of iminobis-(triphenylchlorostibane) confirms the presence of equivalent phenyl groups thereby offering further evidence in support of the imino structure.

During the course of this work it has been shown that iminobis-(trialkylchlorostibanes) readily hydrolyze when exposed to the atmosphere with evolution of ammonia. The hydrolysis reaction is postulated to proceed according to the following equation:

$$[R_3Sb(Cl)]_2NH + H_2O \rightarrow [R_3Sb(Cl)]_2O + NH_3$$

Infrared data are consistent with the proposed anhydride structure in that no absorption is seen for an O-H group and the alkyl-chloro derivatives show the Sb-O-Sb absorption in the 775-743 cm^{-1} region. A weak to medium band, which might be attributed to the Sb-C symmetrical stretching vibration, is seen at 534 cm^{-1} for the methyl compound and at 498 cm^{-1} for the ethyl compound. These bands are not seen for the higher analogues. No definite assignment can be made for the Sb-Cl stretching vibration.

Proton magnetic resonance data are also consistent with that to be expected for the anhydride structure. In other words, only equivalent alkyl groups were shown and no absorption resulting from a proton on oxygen could be found. The spectrum of oxybis-(trimethylchlorostibane) was obtained in both water and chloroform. The spectrum obtained

using water as a solvent showed only one peak whereas the spectrum taken in chloroform showed three peaks, the same as in the case of iminobis-(trimethylchlorostibane).

Molecular weight data were obtained for oxybis-(triethyl- and tri-n-propylchlorostibanes) and are in excellent agreement with the proposed anhydride structure.

Dry iminobis-(triphenylchlorostibane) does not hydrolyze very rapidly when exposed to the atmosphere. However, if the compound is placed in a wet solvent, hydrolysis occurs quite readily. The proton magnetic resonance spectrum of oxybis-(triphenylchlorostibane) is completely consistent with that to be expected for the anhydride structure in that it shows only one kind of phenyl group and no absorption for a proton attached to oxygen.

The use of infrared spectroscopy for determining the existence of an Sb-Cl bond in compounds of the type $[R_3Sb(Cl)]_2O$ did not prove fruitful. In most cases the Sb-Cl absorption was (1) masked by other peaks in the 250-300 cm^{-1} region; (2) very weak and therefore difficult to identify, or (3) below the range of the instrument. As a direct result of these difficulties, a new approach was made which involved the exchange of a chlorine atom for a nitrato group because the type of bonding between antimony and chlorine should be similar to that between antimony and a nitrato group. Actually, the bond between antimony and

chlorine might even be predicted to show more covalent character than the corresponding antimony-nitrato bond, since the Pauling electronegativity for chlorine is less than that for oxygen and the properties of the bond are governed predominantly by the atoms directly connected to one another. Insight might be gained into the nature of the bond through infrared spectroscopy since both the nitrate ion and the partially covalent nitrato group give characteristic infrared absorptions. In particular, the ν_3 vibrational mode (NO_2 stretch) of the nitrate ion, which possesses D_{3h} symmetry, occurs at approximately 1390 cm^{-1}. If the symmetry is lowered as a result of lattice distortion, this mode undergoes a splitting which usually does not exceed 125 cm^{-1} (26). On the other hand, if the symmetry is lowered towards C_{2v} as the result of partial covalent bonding, the splitting exceeds 125 cm^{-1}. The frequency ranges for both of the above mentioned species are conveniently listed in a publication by Addison and Gatehouse (24). It has been suggested by Ferraro (25) that the degree of the $\nu_4 - \nu_1$ splitting might be used as a measure of covalent character in the metal-nitrato bond. The observed splitting can be compared with that obtained for methyl nitrate, which presumably contains a purely covalent nitrato group of C_{2v} symmetry (41).

The following compounds were prepared in order to determine whether or not the $Sb\text{-}ONO_2$ linkage possessed

covalent character: $(CH_3)_3Sb(ONO_2)_2$, $[(C_6H_5)_3Sb(ONO_2)]_2O$, $[(C_2H_5)_5Sb(ONO_2)]_2O$, $(C_6H_5)_4SbONO_2$, and $[(CH_3)_3Sb(ONO_2)]_2O$. As stated earlier, the conclusions of this study would also be presumed to hold for the Sb-Cl bond. This presumption is supported by the fact that the infrared spectrum of trimethyldinitratostibane shows a $\nu_4 - \nu_1$ splitting of 240 cm^{-1} thereby showing the presence of a partially covalent nitrato group. This is entirely consistent with the fact that the infrared spectrum of trimethyldichlorostibane shows an absorption at 277 cm^{-1} which is attributed to the Sb-Cl asymmetrical stretching vibration. That the band at 277 cm^{-1} results from an Sb-Cl vibration is confirmed by the fact that when the chlorine atoms are replaced by bromine atoms the band disappears, but the remainder of the spectrum does not change.

The remainder of the compounds shown above are listed in decreasing order of their $\nu_4 - \nu_1$ splitting. The $\nu_4 - \nu_1$ splitting for oxybis-(triphenylnitratostibane) is 220 cm^{-1}. This is sufficient evidence to conclude that the $Sb-ONO_2$ bond possesses partial covalent character, probably only slightly less than that found in trimethyldinitratostibane. From this data it is assumed that the antimony is bonded directly to the chlorine in oxybis-(triphenylchlorostibane). This conclusion is thoroughly supported by the work of Kolditz et al. (12), who found that the molecular weight of

oxybis-(triphenylchlorostibane) in bromoform agreed with the anhydride structure and that a solution of the compound in acetonitrile shows no electrical conductivity.

Oxybis-(triethylnitratostibane) gives a $\nu_4 - \nu_1$ splitting of 165 cm^{-1} thereby showing a definite lowering of covalent character in the Sb-ONO_2 bond, but not enough to conclude that there is no sharing of electrons in the bond. This conclusion is also carried over to oxybis-(triethylchlorostibane). Molecular weight data for the chloro compound are consistent with the anhydride structure, but are inconclusive concerning the type of bonding since the determination was carried out in benzene. No conductivity data are available.

The remaining two compounds, tetraphenylnitratostibane and oxybis-(trimethylnitratostibane) show a $\nu_4 - \nu_1$ splitting of 139 and 137 cm^{-1}, respectively. The ν_2 mode for the covalent nitrato group shows as a strong peak at 1018 cm^{-1} in the anhydride, but either is missing or is overlapped by the phenyl absorption at 1018 cm^{-1} in the tetraphenyl derivative. The ν_6 mode is undoubtedly masked by the strong Sb-O-Sb absorption at 788 cm^{-1} in the anhydride and is missing in tetraphenylnitratostibane. The similar splitting values probably indicate that the Sb-O-NO_2 linkage still possesses some covalent character, although there seems little doubt that the bond must be highly polar.

It therefore seems reasonable to conclude that the chloro derivatives also contain a highly polar antimony-chlorine bond. Neither molecular weight nor electrical conductivity data are available for either of the above compounds.

X-ray powder patterns were obtained for oxybis-(tri-n-propylchlorostibane) and oxybis-(triphenylchlorostibane) in an attempt to determine the crystal system to which they belong. The former compound gave only one intense peak relative to the others and failed to give any peaks beyond an angle of 18.88°. The latter compound failed to give any intense peaks at all. Not enough lines were obtained from either of these spectra to make possible the necessary calculations involved in a determination of this type.

Recently, Jensen and Nielsen (35) have made available far infrared data on triphenyldibromostibane and triphenyldibromobismuthane. The first compound shows absorptions at 294 and 238 cm^{-1}. Both bands were assigned to Sb-Br vibrations, but our data shows that the 294 cm^{-1} band is present in a large variety of Sb(V) compounds containing phenyl groups and not bromine atoms and therefore must not result from an Sb-Br vibration. The band at 238 cm^{-1} undoubtedly results from the Sb-Br stretching vibration and is conclusive evidence of partial covalent bonding between the antimony and bromine atoms. It is also shown that bismuth is bonded directly to bromine in triphenyldibromo-

bismuthane as the absorption at 219 cm^{-1} must result from the Bi-Br stretching vibration.

Doak (14) presents infrared data for $[(C_6H_5)_3Sb\text{-}O\text{-}Sb(C_6H_5)_3][ClO_4]_2$ and concludes that the perchlorate group is ionic; therefore, the antimony atoms should be tetracovalent exhibiting tetrahedral symmetry instead of trigonal bipyramidal symmetry. This would render both the symmetrical and asymmetrical $Sb\text{-}C_{(ar)}$ stretching vibrations infrared active. Since the above perchlorate is the only one of the compounds included in the study to exhibit a medium intensity band at 411 cm^{-1}, it is concluded that this band probably results from the symmetrical $Sb\text{-}C_{(ar)}$ stretching vibration. The rendering of this particular vibration infrared active might also result from severe distortion of the trigonal bipyramidal symmetry around antimony and it is not unlikely that distortion occurs in compounds of this type. It might bear repeating at this time that imino- and oxybis-(trimethyl- and triethylchlorostibanes) and their nitrato derivatives also exhibit absorptions that might result from the $Sb\text{-}C_{(ar)}$ symmetrical stretching vibration, and these compounds are not considered to be ionic. And finally, tetraphenylstibonium tetraphenylborate, which is undoubtedly a true tetracoordinate antimony compound, does not show any absorption in the 411 cm^{-1} region.

The basic character of oxybis-(trimethylchlorostibane) is clearly demonstrated by the reaction of this compound with concentrated hydrochloric acid to yield trimethyldichlorostibane and water. The reaction is postulated to proceed according to the following equation:

$$[(CH_3)_3Sb(Cl)]_2O_{(aq)} + 2HCl_{(conc)} \rightarrow 2(CH_3)_3SbCl_{2(s)} + H_2O$$

However, it now appears that the above equation is somewhat overly simplified. It has been shown in some of the earlier literature (11,42) that trimethyldihalostibanes hydrolyze extensively in aqueous solution. Long (13) recently reinvestigated some of this earlier work and concluded that indeed the dihalides are probably completely hydrolyzed in aqueous solution, but the reaction is reversible since the dihalides can be recrystallized from water unchanged. It is further stated that the particular product obtained from the aqueous solution must therefore be dependent upon the chloride and hydronium ion concentrations. The following equations were postulated for the formation of the various compounds:

$$(CH_3)_3Sb(OH)_2 + 2X^- + 2H_3O^+ \rightarrow (CH_3)_3SbX_2 + 4H_2O$$

and

$$(CH_3)_3Sb(OH)_2 + X^- + H_3O^+ \rightarrow (CH_3)_3Sb(OH)X + 2H_2O$$

$$\downarrow$$

$$\tfrac{1}{2}[(CH_3)_3Sb(Cl)]_2O + \tfrac{1}{2}H_2O$$

In view of the above information it therefore seems quite reasonable to postulate that oxybis-(trimethylchlorostibane) is also completely hydrolyzed in aqueous solution and the overall reactions probably proceed according to the following equations:

$$\text{I} \quad (CH_3)_3SbO\cdot H_2O + H_3O^+ + Cl^- \rightleftharpoons (CH_3)_3Sb(OH)Cl + 2H_2O$$

$$\text{II} \quad (CH_3)_3Sb(OH)Cl + H_3O^+ + Cl^- \rightleftharpoons (CH_3)_3SbCl_2 + 2H_2O$$

$$\text{III} \quad 2(CH_3)_3Sb(OH)Cl \rightleftharpoons [(CH_3)_3Sb(Cl)]_2O + H_2O$$

The reaction of concentrated hydrochloric acid with oxybis-(trimethylchlorostibane) actually involves all the reactions represented by equations I, II, and III.

The proton magnetic resonance spectrum of aqueous oxybis-(trimethylchlorostibane) shows only one sharp peak thereby indicating the presence of only one species and if that species is the anhydride, the methyl groups must be equivalent. However, it is more probable that the lone peak results from the methyl protons of trimethylstibine oxide monohydrate.

One cannot study the corresponding reactions in aqueous solution for the triphenyl derivatives since all of the compounds in question have very low solubilities in water. However, by simply choosing the appropriate solvent and reaction conditions, one can show that the triphenyl derivatives undergo the same type of reactions as do the

trimethyl derivatives. For instance, triphenyldichlorostibane is partially hydrolyzed to oxybis-(triphenylchlorostibane) by (a) treating an alcoholic solution of the dichloride with boiling water (12), or (b) treating the solid with refluxing water with vigorous stirring for several days. Method (a) is preferred since method (b) is extremely dependent upon the stirring technique. Only when the dichloride is treated with a boiling aqueous solution of hydroxide ion is complete hydrolysis to triphenylstibine oxide accomplished.

The basic character of oxybis-(triphenylchlorostibane) is established by its reaction with gaseous hydrogen chloride in dry benzene to form triphenyldichlorostibane, and there is little doubt that triphenylstibine oxide would also undergo a similar reaction. As a matter of fact, triphenyldiacetatostibane is prepared in this manner (7,43).

That antimony has a considerable affinity for oxygen is verified by the fact that upon pyrolysis of oxybis-(trimethylchlorostibane), antimony(III) oxide is obtained as a major product along with trimethylstibine and methyl chloride. The reaction is postulated to proceed according to the following equations:

$$[(CH_3)_3Sb(Cl)]_2O \xrightarrow{\Delta} 2CH_3Cl + [(CH_3)_2Sb]_2O$$

$$3[(CH_3)_2Sb]_2O \xrightarrow{\Delta} Sb_2O_3 + 4(CH_3)_3Sb$$

The experimental conditions were such that there was no visual evidence for the intermediate formation of oxybis-(trimethylstibine), which is a liquid (18). The above alkyl halide elimination reaction is analogous to the standard preparation of dialkylhalostibines by pyrolyzing the corresponding trialkyldihalostibanes (9,18). Accordingly, tri-n-butyldichlorostibane, which readily distills under high vacuum, was pyrolyzed at higher pressure. A very low boiling liquid was obtained, which is believed to be n-butyl chloride, along with an orange, high-boiling material. This orange liquid is almost certain to be di-n-butylchlorostibine. The liquid decomposes with deposition of a black solid very soon after distillation is complete. The reason for the decomposition is not known. The black solid, which was first thought to be metallic antimony, is probably the black polymeric n-butylstibine described by Herbstman (44). The preparation of tri-n-butyldichlorostibane is analogous to the reaction of various tertiary phosphines with phosphorus(III) chloride.

CHAPTER III

THE SYNTHESIS OF ANTIMONY-NITROGEN COMPOUNDS BY AMMONOLYSIS

Experimental

Manipulation of materials

Triphenyldichlorostibane was purchased from Peninsular ChemResearch, Inc. and was recrystallized from ethyl acetate before use. The material melted at 143-144°C. Tetraphenylbromostibane was purchased from Alfa Inorganics, Inc. and used as received. The material melted at 210-213°C. Liquid ammonia solutions of potassium amide were sometimes generated *in situ* and other times generated from freshly prepared potassium amide. The liquid ammonia was dried with sodium before being used. All liquid ammonia reactions were carried out on a vacuum line with rigorous exclusion of water. Reagent grade solvents were dried with calcium hydride. Technical grade solvents were distilled from calcium hydride and then stored over the same drying agent in a dry box. All resulting compounds were purified and stored in a dry box using glassware that had been baked at 150°C. for more than one hour and thoroughly evacuated for over 15 minutes while hot.

Analytical methods

Elementary analyses were carried out by Schwarzkopf Microanalytical Laboratory, Woodside, New York and Galbraith Laboratories, Inc., Knoxville, Tennessee. Some nitrogen analyses were performed in this laboratory using a Coleman Model 29 Nitrogen Analyzer.

Melting points were obtained using wax sealed capillaries on a Thomas-Hoover capillary melting point apparatus and are uncorrected.

Infrared spectra were obtained on a Beckmann Model IR 10 infrared spectrophotometer using cesium iodide optics. Solid state spectra were obtained using Nujol and Kel-F mulls. All samples were prepared in a dry box and stored in a dessicator until being placed on the instrument. Infrared spectral absorption frequencies are listed in Table 3.

Proton magnetic resonance spectra were obtained on a Varian nuclear magnetic resonance analytical spectrometer Model A60-A. All spectra were obtained in deutero-chloroform containing a small amount of tetramethylsilane. The mixture was dried over calcium hydride. In some cases benzene was also added to the chloroform to act as an internal reference to facilitate the calculation of the chemical shift of the phenyl groups from the benzene signal. Proton magnetic resonance data are compiled in Table 7.

TABLE 3

INFRARED SPECTRAL DATA, Cm^{-1} [a]

88% $[(C_6H_5)_3Sb{=}N{=}Sb(C_6H_5)_3]Cl$ + 12% $[(C_6H_5)_3Sb(Cl)]_2NH$ Nujol	3050(w),2200(w),1955(vw,b), 1880(vw,b),1810(vw,b),1570(w), 1478(s),1430(vs),1330(w), 1300(w),1263(vvw),1180(w), 1158(w),1068(s),1020(m),998(s), 912(vvw),870(s),854(vs),765(w), 734(vs),690(vs),660(w),613(vvw), 510(m),453(s),440(m,sh),278(w)
$[(C_6H_5)_3Sb{=}N{=}Sb(C_6H_5)_3]Cl_2K$ $0.8C_7H_8$ Nujol	3050(w),2195(m),1955(vvw,b), 1875(vvw,b),1810(vvw,b),1572(w), 1492(w,sh),1478(s),1432(vs), 1330(w),1302(w),1263(vvw), 1182(w),1158(vw),1068(s), 1020(w),998(m),970(vvw),910(vvw), 878(s,sh),860(vs),735(vs), 692(vs),660(w),612(vvw),510(m), 460(s,sh),454(s),442(m)
$(C_6H_5)_5Sb$ Nujol	3125(vvw),3050(m),3000(w), 1950(vw,b),1880(vw,b),1810(vw), 1565(w),1470(m),1422(vs), 1330(vvw),1300(w),1260(w), 1185(w),1150(w),1095(vvw), 1070(m),1050(s,d),1018(vw), 996(s),968(vvw),910(vvw), 850(vvw,d),800(w,b),729(vs,d), 696(vs,d),640(w),611(vvw), 470(s),452(s),442(s)
$(C_6H_5)_3SbCl_2 \cdot N(CH_3)_3$ Kel-F, Nujol	3050(m),3000(m),2950(m,b), 2665(s,b),2500(s,b),1950(vvw,b), 1885(vw,b),1810(w,b),1570(s), 1475(s),1430(s),1410(vw), 1378(vw),1330(w),1302(w), 1260(w),1240(vw,sh),1180(m), 1158(w),1062(m),1029(m),992(vs), 915(vw),845(vvw),760(vs), 735(vs),688(vs),612(vw),452(vs), 280(m)

[a] s, strong; m, medium; w, weak; sh, shoulder; b, broad; d, doublet; v, very.

Reaction of triphenyldichlorostibane with liquid ammonia

$$(C_6H_5)_3SbCl_{2(s)} \xrightarrow{NH_{3(l)}} x[(C_6H_5)_3Sb(Cl)]_2NH + y[(C_6H_5)_3Sb{=}N{=}Sb(C_6H_5)_3^+]Cl^- + zNH_4Cl$$

Triphenyldichlorostibane, 4.72 mmoles, was stirred in excess sodium-dried liquid ammonia for five yours at -60 to -70°C. The reaction was carried out on a vacuum line to insure rigorous exclusion of moisture. The excess ammonia was removed from the flask under vacuum and the sealed flask was transferred to a dry box. The solid was treated with about five milliliters of boiling benzene which dissolved all but 0.02 gram. The insoluble material did not melt under 320°C., sublimed, and was water soluble. This solid was assumed to be ammonium chloride. Upon cooling to room temperature the benzene yielded 0.17 gram of a white solid that softened slightly at 220°C. and melted at 270°C. with decomposition.

The reaction product is soluble in hot benzene and chloroform and readily hydrolyzes with evolution of ammonia when exposed to the atmosphere. The infrared spectrum of the product is shown in Figure 50. The weak peak at 765 cm^{-1} is attributed to the Sb-NH-Sb vibration and the very strong peak at 854 cm^{-1} to the Sb=N=Sb vibration. The analytical results and the infrared data indicate that the product is

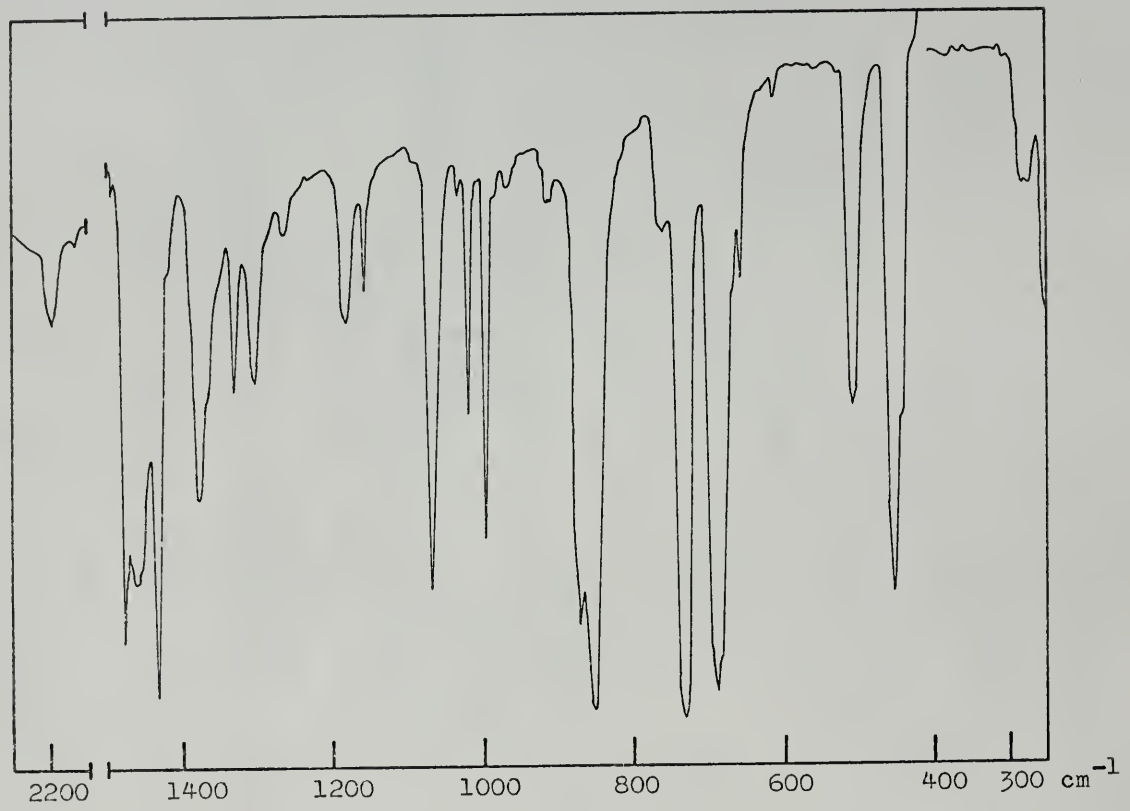


Fig. 50.-Infrared spectrum of a mixture $[(C_6H_5)_3Sb{=}N{=}Sb(C_6H_5)_3]Cl$ (88%) and $[(C_6H_5)_3Sb(Cl)]_2NH$ (12%).

a mixture of 88 per cent $[(C_6H_5)_3Sb{=}N{=}Sb(C_6H_5)_3^+]Cl^-$ and 12 per cent $[(C_6H_5)_3Sb(Cl)]_2NH$.

Anal. Calcd. for the above mixture: C, 56.89; H, 3.99; N, 1.84; Cl, 5.22. Found: C, 57.09; H, 4.02; N, 1.85; Cl, 5.23.

The benzene solution was evaporated to dryness leaving 1.5 grams (3.54 mmole) of unreacted triphenyldichlorostibane as residue.

If the above reaction is allowed to proceed for several days at temperatures between -70° and -78°C. approximately the same weight of product is obtained. However, the ratio of the components of the mixture changes to 75 per cent $[(C_6H_5)_3Sb{=}N{=}Sb(C_6H_5)_3^+]Cl^-$ and 25 per cent $[(C_6H_5)_3Sb(Cl)]_2NH$. The infrared spectrum, which is shown in Figure 51, shows an increase in intensity of the 765 cm^{-1} peak (Sb-NH-Sb) and a decrease in intensity of the 854 cm^{-1} peak ($Sb{=}N{=}Sb$). A second crop of crystals obtained from the benzene was found to melt at 221.5-223.5°C. The infrared spectrum of this material was identical with that of iminobis-(triphenylchlorostibane) and a mixed melting point determination showed no depression. Regardless of reaction time, a large mechanical loss accounts for low yields of about 17 per cent based on antimony.

Proton magnetic resonance data were not obtained.

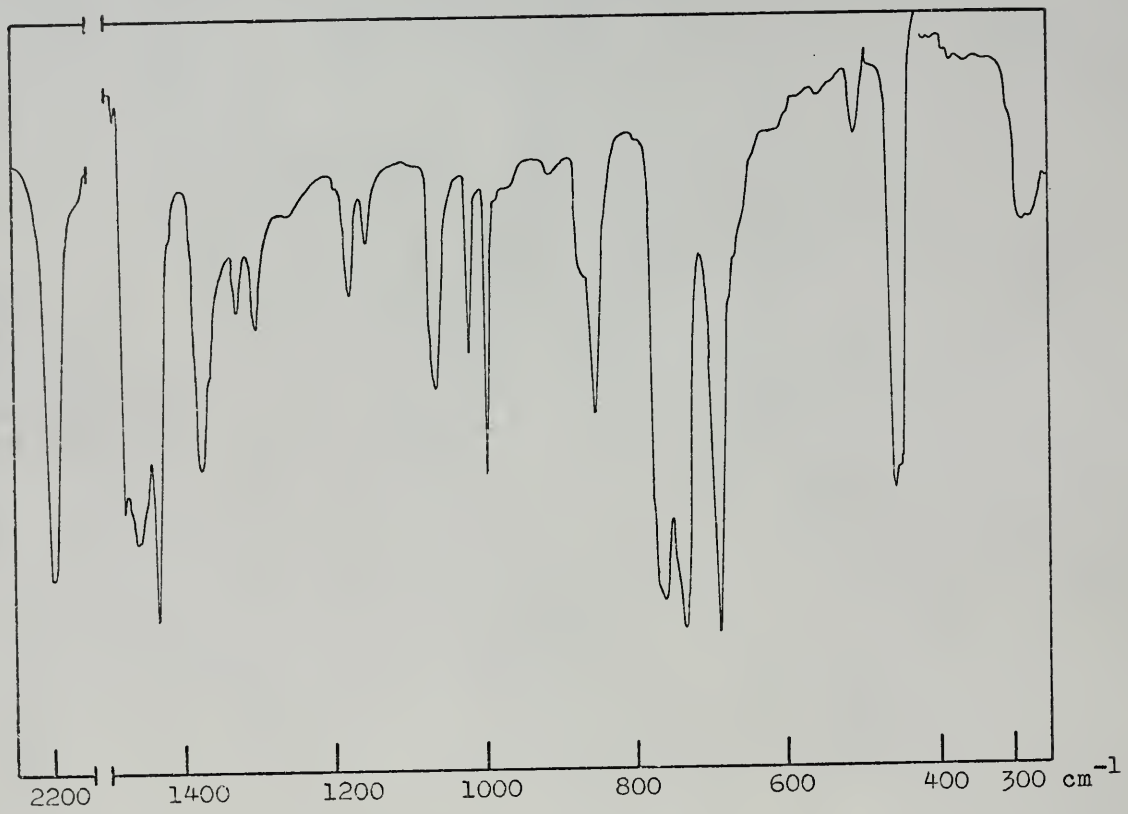


Fig. 51.-Infrared spectrum of a mixture $[(C_6H_5)_3Sb{=}N{=}Sb(C_6H_5)_3]Cl$ (75%) and $[(C_6H_5)_3Sb(Cl)]_2NH$ (25%).

Reaction of triphenyldichlorostibane with potassium amide in $NH_{3(l)}$

In a typical vacuum line experiment, 0.55 gram (14 mmoles) of potassium was slowly added to sodium dried liquid ammonia in which a small amount of iron(III) chloride had been dissolved. The formation of potassium amide was assumed to be complete when the color of the solution changed from dark blue to yellow-green and gas evolution was complete. After the non-condensible gas was removed from the system, triphenyldichlorostibane, 6.5 mmoles, was slowly added from a tipping tube with vigorous stirring. The color of the solution gradually faded until the ammonia was colorless and contained an insoluble white solid. The ammonia was removed by vacuum and the sealed reaction flask was transferred to a dry box.

The white solid was extracted with several 10 milliliter portions of boiling toluene. The toluene-insoluble material was dried by vacuum and found to weigh 0.54 gram. The material was assumed to be potassium chloride. During the extraction process the toluene became colored deep brown and upon cooling yielded 1.2 grams of a tan solid that softened slightly at 210°C. and melted at 255-260°C. with decomposition. The oily residue obtained upon evaporation of the toluene appeared to be decomposition products. Infrared data from this oil did not show any familiar Sb-N absorptions and did not evolve ammonia when exposed to the

atmosphere. The yield of $[(C_6H_5)_3Sb{=}N{=}Sb(C_6H_5)_3]Cl_2K\cdot 0.8C_7H_8$ was 40 per cent of theory based on triphenyldichlorostibane.

$[(C_6H_5)_3Sb{=}N{=}Sb(C_6H_5)_3]Cl_2K\cdot 0.8C_7H_8$ is soluble in chloroform and boiling toluene (with some reaction) and hydrolyzes very rapidly when exposed to moisture. The infrared spectrum of the compound is shown in Figure 52. The peak at 860 cm^{-1} is attributed to the Sb=N=Sb linkage.

Anal. Calcd. for $[(C_6H_5)_3Sb{=}N{=}Sb(C_6H_5)_3]Cl_2K\cdot 0.8C_7H_8$: C, 55.28; H, 4.06; N, 1.55; Cl, 7.84. Found: C, 55.18; H, 4.06; N, 1.63; Cl, 7.82.

Figure 53 shows the proton magnetic resonance spectrum of $[(C_6H_5)_3Sb{=}N{=}Sb(C_6H_5)_3]Cl_2K\cdot 0.8C_7H_8$. The peak labelled A is assigned to the ortho protons of the phenyl group and peak A' to the meta and para protons. The phenyl protons from toluene are mixed with peak A'. Peak B is assigned to the methyl protons of toluene. The ortho proton pattern is shifted -27.7 cps from the benzene signal whereas the two tallest peaks of the meta and para proton pattern lie symmetrically around the benzene signal. The area ratio of peak A to A' is approximately 2 to 3 after all areas corresponding to the toluene phenyl protons is subtracted from peak A'. The toluene could not be removed from the compound even after 16 hours under high vacuum at 50°C.

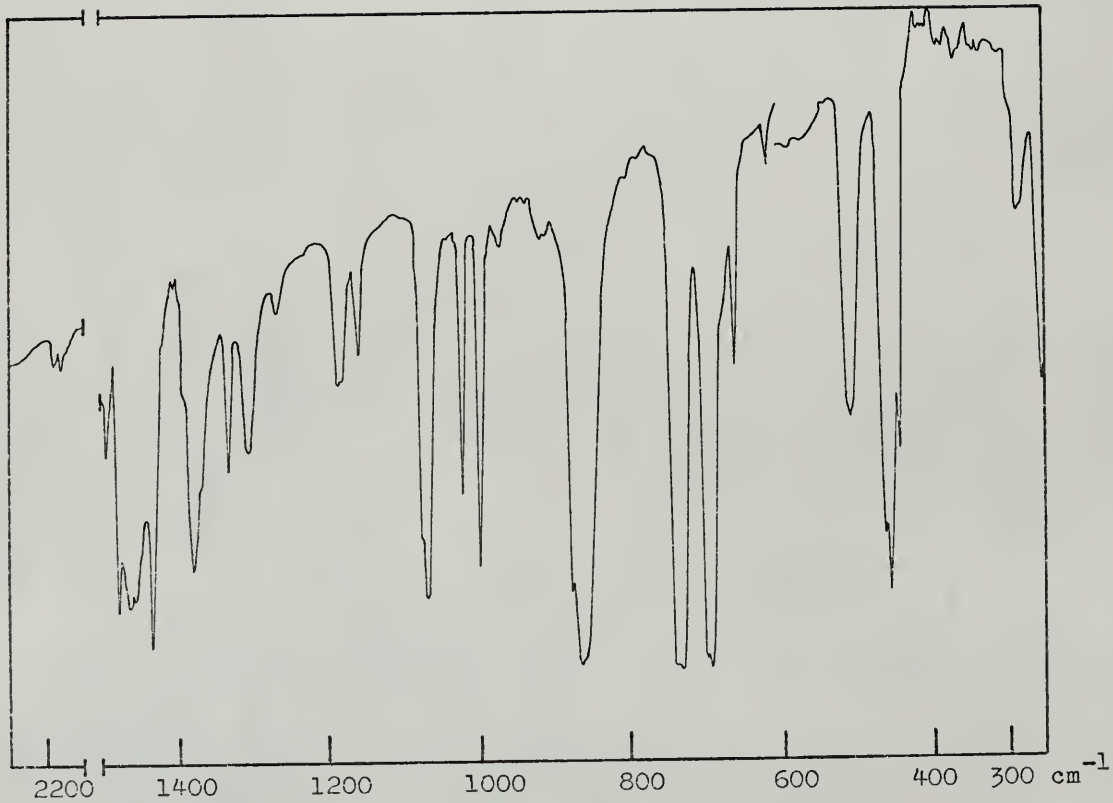


Fig. 52.-Infrared spectrum of $[(C_6H_5)_3Sb{=}N{=}Sb(C_6H_5)_3]Cl_2K \cdot 0.8C_7H_8$.

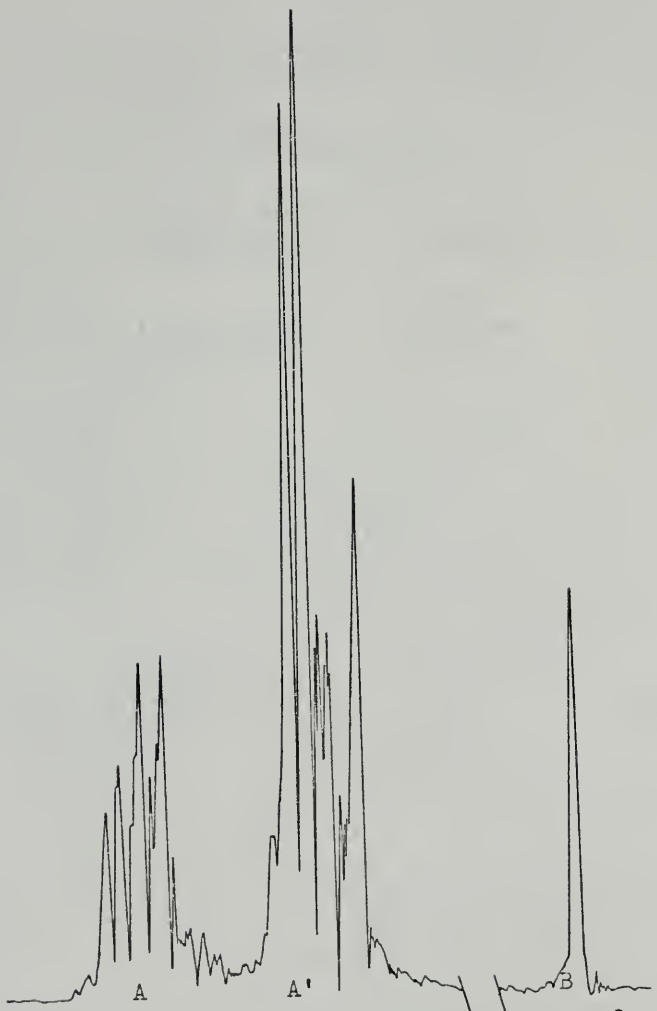


Fig. 53.-Proton magnetic resonance spectrum of $[(C_6H_5)_3Sb{=}N{=}Sb(C_6H_5)_3]Cl_2K{\cdot}0.8C_7H_8$.

The reaction was repeated using a 1:1.5 mole ratio of triphenyldichlorostibane to potassium amide. The product was recrystallized from toluene and melted around 250°C. The solid was mixed with the product of the previous experiment and again recrystallized from toluene. The toluene discolored and some decomposition was evident. The recrystallized solid softened around 220°C. and melted with decomposition at 255-257°C. The infrared spectrum is similar to that shown in Figure 52.

The analytical results suggest a compound of the type $\left\{(C_6H_5)_3Sb{=}N\text{-}\left[\text{-}Sb(C_6H_5)_3\text{-}N{=}\right]_{0.73}{=}Sb(C_6H_5)_3\right\}0.27Cl\cdot0.42KCl$. However, this is purely speculative and is not confirmed by molecular weight data.

Anal. Calcd. for $\left\{(C_6H_5)_3Sb{=}N\text{-}\left[\text{-}Sb(C_6H_5)_3\text{-}N{=}\right]_{0.73}{=}Sb(C_6H_5)_3\right\}0.27Cl\cdot0.42KCl$: C, 57.32; H, 4.02; N, 2.35; Sb, 32.33; Cl, 2.38; K, 1.60. Found: C, 56.83; H, 4.04; N, 2.34; Sb, 32.22; Cl, 2.36; K, 0.96.

The proton magnetic resonance spectrum is similar to that shown in Figure 53.

A deficiency of potassium amide, less than a 1:1.5 mole ratio of triphenyldichlorostibane to potassium amide, in a reaction similar to that mentioned above leads to an even more complex mixture. The mixture (A) was recrystallized

from toluene and melted at 266-269°C. with decomposition. Infrared data show the presence of an Sb-NH-Sb linkage along with the Sb=N-Sb linkage. Elemental analyses give a N:Cl ratio of 1:1.66. Antimony analysis was not performed. It is probable that the mixture contains $[(C_6H_5)_3Sb(Cl)]_2NH$ and a compound similar to $\left\{(C_6H_5)_3Sb{=}N{-}\left[Sb(C_6H_5)_3{-}N{=}\right]_{1-x}Sb(C_6H_5)_3\right\}xCl\cdot zKCl$. Pure imino-bis-(triphenylchlorostibane) was isolated from the toluene as a second crop.

Mixture (A) was stored for about four months in a dry atmosphere at about 30°C. The infrared spectra of both the freshly prepared and the stored samples were similar, but the melting points were quite different. The freshly prepared compound melted at 266-269°C. and the stored sample melted at 154-159°C. The elemental analysis of the stored sample showed an Sb:N:Cl ratio of 1.59:1.00:0.61. The composition apparently changed with time.

The reaction of triphenyldichlorostibane with potassium amide in liquid ammonia was repeated. The stibane (4.72 mmoles) was slurried with liquid ammonia and powdered potassium amide (7.15 mmoles) was slowly added from a tipping tube with vigorous stirring. The temperature of the reaction vessel was maintained between -50 and -60°C. The contents of the flask were stirred for about two hours at

this temperature and then the excess ammonia was removed by vacuum. Prolonged high vacuum treatment was required for complete removal of ammonia.

In an inert atmosphere the white solid was treated with 5 milliliters of toluene. It appeared that some of the solid dissolved, but upon application of heat precipitation occurred with the formation of a solid cake in the flask. More toluene was added and the solid was extracted with the boiling solvent. Several more extractions were required to remove all soluble material from the insoluble solid which was assumed to be potassium chloride.

Evaporation of the discolored toluene yielded 1.44 grams of a tan solid (I) that melted in the 260-270°C. range. The infrared spectrum of (I) shows bands at 860, 765 and 510 cm^{-1}, thereby indicating the presence of Sb-N-Sb and Sb-NH-Sb linkages. No yield data were recorded since the purpose of the experiment was to separate and identify as many of the reaction products as possible.

A second recrystallization of a small portion of (I) from toluene yielded a tan solid which softened at 174°C. and melted at 255-258°C. with decomposition. The infrared spectrum of the twice recrystallized material is the same as that shown in Figure 52. The Sb-NH-Sb absorption at 765 cm^{-1} does not show and it is presumed that all iminobis-(triphenylchlorostibane) has been removed by fractional

crystallization. Analytical results are consistent with a compound of the type

$$\left\{(C_6H_5)_3Sb{=}N{-}\left[Sb(C_6H_5)_3{-}N\right]_{1.5}{=}Sb(C_6H_5)_3\right\}0.5Cl.$$

Anal. Calcd. for the above compound: C, 58.72; H, 4.11; N, 2.72; Sb, 30.07; Cl, 1.38. Found: C, 58.00; H, 4.06; N, 2.69; Sb, 32.75; Cl, 2.54.

The remainder of product (I) was treated with excess potassium amide in liquid ammonia at -50 to -60°C. for two hours. The infrared spectrum of the crude product shows a weak band at 860 cm^{-1}, a medium intensity doublet at 660 and 645 cm^{-1}, and a strong band at 478 cm^{-1}. The latter two bands are unfamiliar, but might well result from the Sb-NH absorption of triphenylstibine imine. Triphenylstibine imine is a known compound, but no reliable infrared data are available. The crude solid decomposed sharply at 148°C.

About one half of the crude solid was recrystallized from boiling toluene. The material melted at 255-259°C. with decomposition and is assumed to be a product similar to that obtained in previous experiments. The infrared spectrum is consistent with that shown in Figure 52. The toluene residue was a sticky tan solid. The infrared spectrum of this sticky solid shows a medium band at 860 cm^{-1} and a medium doublet at 660 and 630 cm^{-1}. The above

bands are of medium intensity with respect to the phenyl absorptions in the 700 cm^{-1} region and it therefore appears that decomposition or further reaction occurred during the recrystallization.

The remaining half of the crude reaction product was purified by precipitation from anhydrous chloroform at room temperature. The chloroform became dark brown in color during the dissolution process even though no heat was applied. Precipitation was induced by adding a large volume of petroleum ether and allowing the solution to stand for several hours. The resulting tan solid melted at 255-257°C. with decomposition. The solid did not show any signs of decomposition until about 10 degrees under the melting point. The infrared spectrum of this sample shows peaks at 860 and 510 cm^{-1} similar to previous reaction products. The analytical results correspond closely with a compound of the type $(C_6H_5)_3Sb{=}N{-}{-}{-}Sb(C_6H_5)_3{-}{-}N\ Sb(C_6H_5)_3\ 0.55Cl{\cdot}0.22KCl$.
0.45

Anal. Calcd. for the above molecule: C, 57.48; H, 4.01; N, 2.21; Sb, 32.40; Cl, 2.96; K, 0.94. Found: C, 57.96; H, 4.06; N, 2.22; Sb, 32.72; Cl, 1.66; K, 1.37.

Proton magnetic resonance data were not obtained.

An additional reaction was performed with a potassium amide-triphenyldichlorostibane mole ratio of 2:1, a large volume of liquid ammonia, and the reaction time extended to

three days. The temperature was always maintained between -50 and -78°C.

An infrared spectrum of the crude reaction product, shown in Figure 54, shows the characteristic peaks of the phenyl groups along with an N-H stretching vibration at 3360 cm^{-1} (weak), a strong doublet at 660 and 645 cm^{-1}, and a strong peak at 478 cm^{-1}. The latter two bands are postulated to result from the Sb-NH linkage of triphenylstibine imine. The infrared spectrum of triphenylstibine oxide has absorptions occurring at 660 cm^{-1}, strong and broad, and 463 cm^{-1}, strong, which probably result from the Sb-O asymmetrical and symmetrical stretching vibrations. It is reasonable to assume that the Sb-NH absorptions will occur very close to the Sb-O absorptions.

Recrystallization of the crude product from a chloroform-petroleum ether mixture apparently causes a reaction to occur as the tan solid obtained from the solvent melted at 255-257°C. and the infrared spectrum differed from that of the crude product. Strong bands occurred at 860 and 510 cm^{-1}, while the peaks at 3360, 660, 645, and 478 cm^{-1} disappeared.

No analytical data were obtained and the proton magnetic resonance spectrum was not recorded.

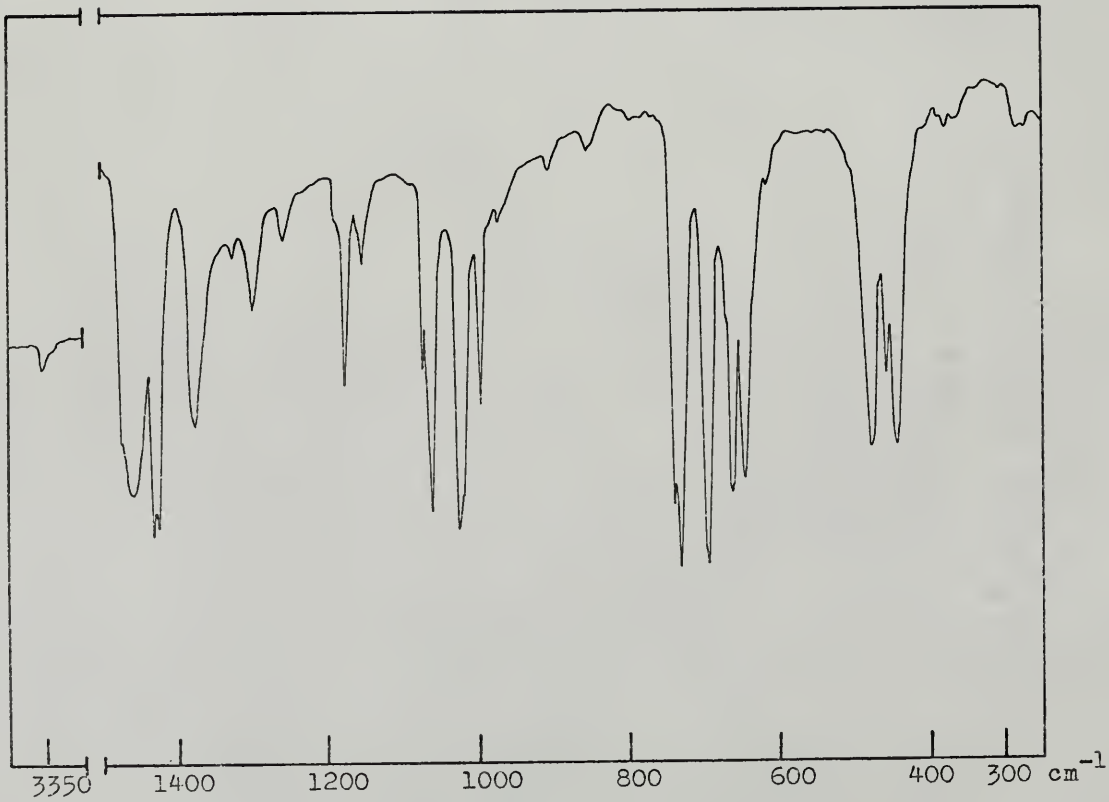


Fig. 54.-Infrared spectrum of the crude product from the ammonolysis of triphenyldichlorostibane.

Reaction of tetraphenylbromostibane with potassium amide in $NH_3(l)$

Tetraphenylbromostibane was reacted with potassium amide in liquid ammonia. The reaction appears to be quite complicated and the results are incomplete. The reaction was carried out twice utilizing different reaction conditions in each case. These reactions are briefly outlined below and the preliminary results are stated.

The first reaction was carried out by slowly adding powdered tetraphenylbromostibane to a liquid ammonia solution of potassium amide with vigorous stirring. The gray solid obtained from the reaction was treated with boiling toluene in an inert atmosphere. This appeared to cause decomposition as the toluene darkened and a black solid was left as residue after the toluene was evaporated to dryness.

A white material was extracted from the black residue with petroleum ether and after recrystallization from alcohol melted at 165-167°C. The compound is identified as pentaphenylstibane and the infrared spectrum is shown in Figure 55. The yield of pentaphenylstibane was about 10 per cent based on antimony.

Anal. Calcd. for $(C_6H_5)_5Sb$: C, 71.03; H, 4.97; Sb, 24.00. Found: C, 70.89; H, 5.12; Sb, 24.37.

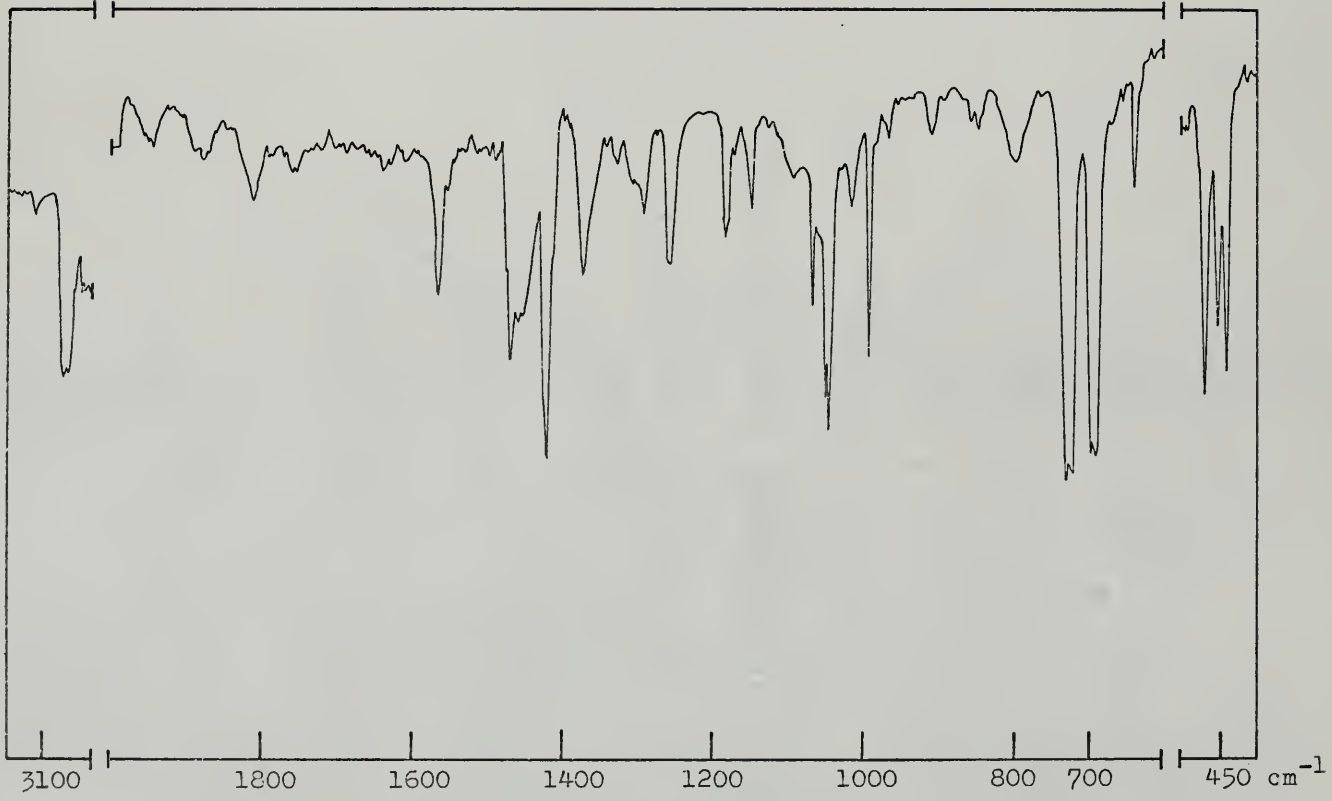


Fig. 55.-Infrared spectrum of $(C_6H_5)_5Sb$.

The proton magnetic resonance spectrum of pentaphenylstibane is shown in Figure 56. The spectrum shows one complex signal which results from the protons on the phenyl groups. The chemical shift values for the ortho, meta, and para protons are similar and the overall peak is situated symmetrically around the benzene signal.

The total reaction product, minus the extracted pentaphenylstibane, was analyzed by thin layer chromatography and found to be a mixture containing at least six components of which one was pentaphenylstibane. Column chromatography afforded the separation of a component that melted at 54-55°C. and was identified as triphenylstibine. The infrared spectrum of this product was consistent with that of the authentic compound and a mixed melting point determination showed no depression. The yield of triphenylstibine was not obtained and no other components were identified.

The second reaction was carried out by adding freshly prepared potassium amide to a liquid ammonia slurry of tetraphenylbromostibane. The solid obtained from the reaction was treated with low boiling petroleum ether. The petroleum ether was evaporated to dryness leaving a solid residue that melted at 167-169°C. after recrystallization from alcohol. The compound is identified as pentaphenylstibane and was obtained in 10 to 15 per cent yield.

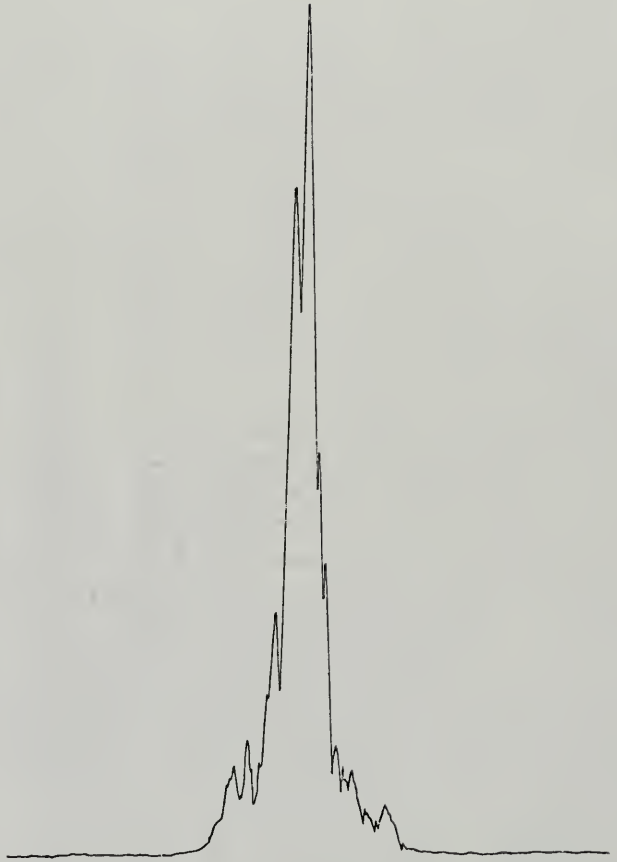


Fig. 56.-Proton magnetic resonance spectrum of $(C_6H_5)_5Sb$.

The petroleum ether insoluble material was exposed to the atmosphere and ammonia evolution was evident. The solid was separated from potassium bromide with carbon tetrachloride. Triphenylstibine oxide hydrate was obtained from the carbon tetrachloride residue in about 10 to 15 per cent yield. The oxide melted at 211-214°C. and the infrared spectrum was consistent with that from an authentic sample. No other products were identified.

Reaction of triphenyldichlorostibane with trimethylamine

$$(C_6H_5)_3SbCl_{2(soln)} + (CH_3)_3N_{(g)} \rightarrow (C_6H_5)_3SbCl_2 \cdot N(CH_3)_{3(s)}$$

Gaseous trimethylamine, 0.17 mole, was passed directly through a benzene (75 ml) solution of triphenyldichlorostibane, 4 mmoles, for one hour. Heat was evolved and precipitation of a solid occurred after about forty-five minutes.

The sealed reaction flask was placed in a dry glove bag and allowed to stand for two days after which the solid was filtered free of solvent. The solid was washed several times with fresh anhydrous benzene and dried by vacuum for four hours. The solid weighed 1.0 gram and melted at 141-147°C. with bubbling.

The hygroscopic reaction product is soluble in chloroform and insoluble in benzene. The yield of the adduct was 47 per cent of theory based on the above equation. The infrared spectrum of $(C_6H_5)_3SbCl_2 \cdot N(CH_3)_3$ is shown in Figure 57.

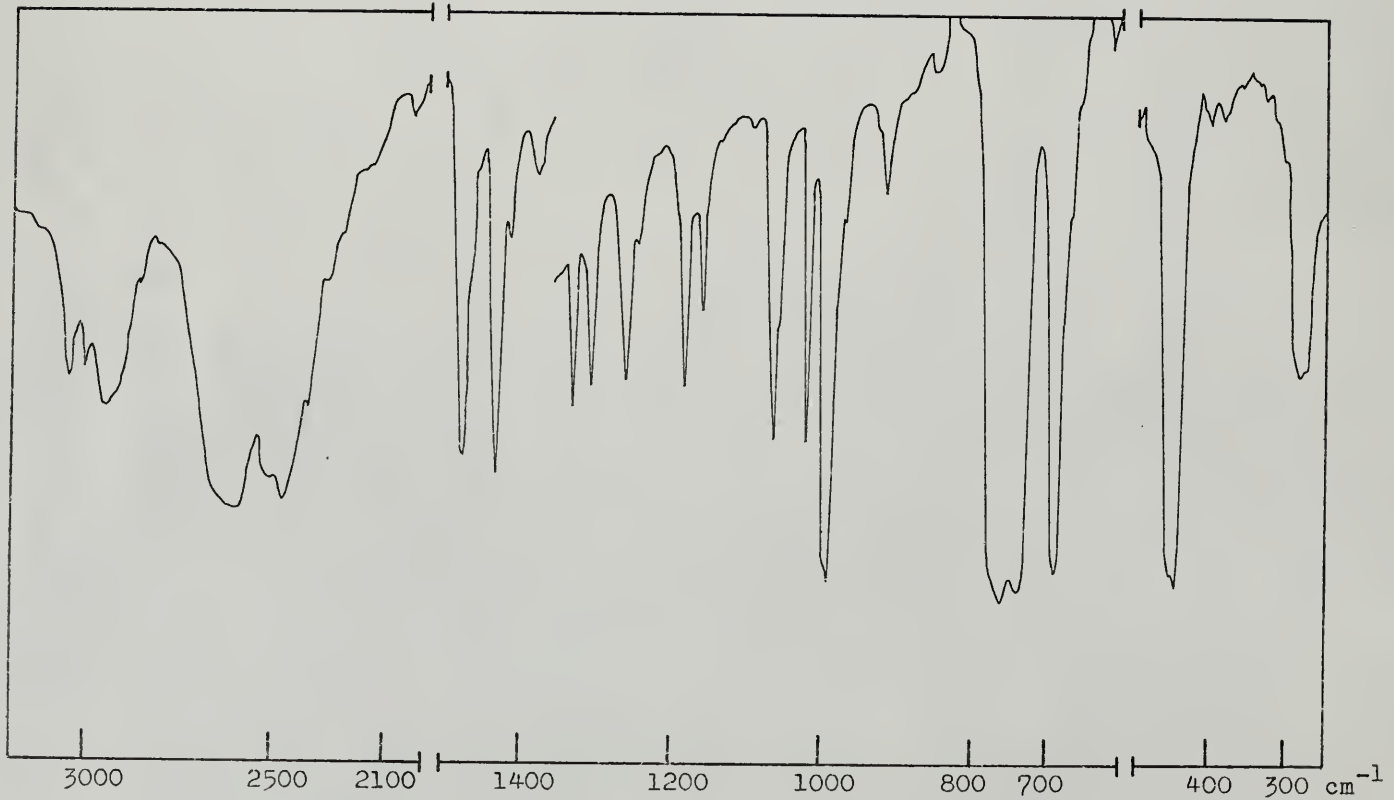


Fig. 57.-Infrared spectrum of $(C_6H_5)_3SbCl_2 \cdot N(CH_3)_3$.

Anal. Calcd. for $(C_6H_5)_3SbCl_2N(CH_3)_3$: C, 52.21; H, 5.01; N, 2.90; Sb, 25.20; Cl, 14.68. Found: C, 52.17; H, 5.20; N, 3.00; Sb, 25.38; Cl, 14.65.

The proton magnetic resonance spectrum of the triphenyldichlorostibane-trimethylamine adduct is shown in Figure 58. The peaks labelled A and B result from the phenyl protons and probably represents two kinds of phenyl groups. The peak labelled C results from the methyl protons of the trimethylamine moiety. The area ratio is within experimental error of the expected 1:1.7 ratio.

Discussion

The main purpose of this work was to study the low-temperature ammonolysis of some halostibanes with the ultimate objective of obtaining some new and interesting Sb-N compounds. During the course of this work Appel and co-workers (10) released a technical report describing the ammonolysis of compounds of the type $(C_6H_5)_3SbX_2$ (X = Cl and Br) with liquid ammonia solutions of sodium and potassium amide. The reactions were carried out in a glass bomb and heat was applied. Triphenylstibine imine was obtained in excellent yields and it was also found that this imine could be condensed to give $(C_6H_5)_3Sb{=}N{-}Sb(C_6H_5)_3{-}N{=}Sb(C_6H_5)_3$ by the simple adjustment of reaction conditions.

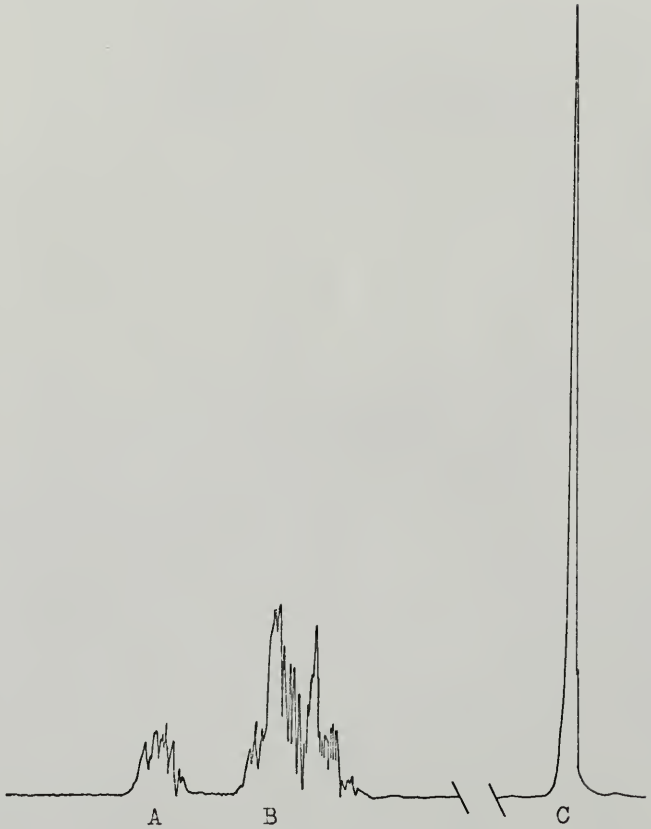


Fig. 58.-Proton magnetic resonance spectrum of $(C_6H_5)_3SbCl_2 \cdot N(CH_3)_3$.

The results obtained from this low temperature work clearly show that less vigorous reaction conditions lead to compounds that are intermediate in nature. The data obtained suggest a reaction that can best be represented by the following equation:

$$(3-x)(C_6H_5)_3SbCl_2 + (6-3x)NH_2^- + (6-3x)K^+ \xrightarrow{NH_3(l)}$$

$$\left\{(C_6H_5)_3Sb{=}N{-}\left[{-}Sb(C_6H_5)_3{-}N{=}\right]_{1-x}Sb(C_6H_5)_3\right\}xCl \; zKCl + (6-3x-z)KCl + (4-2x)NH_3 .$$

The products from the various reactions give the same melting point of 255-257°C. and identical infrared spectra, yet the elemental analyses are not alike for any two products. At this time molecular weight data are not available because of the extreme sensitivity of the product towards moisture and limited solubility in the more common solvents used for molecular weight determinations. Not only does the elemental composition appear to change with time, but also, it appears to change during the purification process. The heat involved in recrystallization from toluene probably causes further reaction to occur; however no heat is applied when chloroform is used and a similar change takes place. Attempts to purify the crude reaction product always lead to a material that absorbs at 860 and 510 cm^{-1} in the infrared spectrum.

Reactions that might occur when triphenyldichlorostibane is mixed with liquid ammonia at low temperature are represented by the equations shown below:

I $(C_6H_5)_3SbCl_2 + 2NH_3 \rightarrow (C_6H_5)_3Sb(NH_2)Cl + NH_4^+ + Cl^-$

II $(C_6H_5)_3Sb(NH_2)Cl + NH_3 \rightarrow (C_6H_5)_3Sb{=}NH\ (A) + NH_4^+ + Cl^-$

III $(C_6H_5)_3Sb{=}NH + (C_6H_5)_3Sb(NH_2)Cl \rightarrow$

$[(C_6H_5)_3Sb{=}N{-}Sb(C_6H_5)_3]Cl\ (B) + NH_3$

IV $2(C_6H_5)_3Sb(NH_2)Cl \rightarrow [(C_6H_5)_3Sb(Cl)]_2NH\ (C) + NH_3$

V $[(C_6H_5)_3Sb{=}N{-}Sb(C_6H_5)_3]Cl + NH_4^+ + Cl^- \rightarrow$

$[(C_6H_5)_3Sb(Cl)]_2NH + NH_3$

VI $[(C_6H_5)_3Sb(Cl)]_2NH + NH_4^+ + Cl^- \rightarrow$

$(C_6H_5)_3SbCl_2 + (C_6H_5)_3Sb(NH_2)Cl + NH_3$

VII $(C_6H_5)_3Sb{=}NH + (C_6H_5)_3SbCl_2 \rightarrow [(C_6H_5)_3Sb(Cl)]_2NH$

The fact that reaction occurs only to a slight extent probably is a result of increasing ammonium ion concentration. The acidic ammonium ion readily attacks the basic nitrogen attached to the antimony atom thereby reversing equations I and II and possibly causing VI to occur. Only products (B) and (C) have been isolated; therefore, the triphenylstibine imine from reaction II, if it is ever present, must be entirely used up in reactions such as III or VII. The compounds obtained from this low temperature ammonolysis are consistent with the low temperature ammonolysis of

triphenyldichloroarsane in which $[(C_6H_5)_3AsNH_2]Cl$ and $[(C_6H_5)_3As{=}N{=}As(C_6H_5)_3]Cl$ are obtained (5). Ammonolysis in chloroform at room temperature yields only the second product shown above. Triphenyldichlorostibane dissolved in benzene does not react with gaseous ammonia at room temperature or slightly above.

The equilibria shown above should be greatly effected by the introduction of a strong base such as amide ion. The initial reaction is postulated to occur between amide ion and ammonium ion, but must also involve other species since data indicate that iminobis-(triphenylchlorostibane) is removed from the reaction mixture by treatment with excess potassium amide. The reaction might be represented by the following equation:

$$[(C_6H_5)_3Sb(Cl)]_2NH + NH_2^- + K^+ \rightarrow$$

$$[(C_6H_5)_3Sb{=}N{=}Sb(C_6H_5)_3]Cl \cdot KCl + NH_3$$

It has been shown that iminobis-(triphenylchlorostibane) does not react with liquid ammonia to any noticeable degree and, in fact, appears to be rather unreactive except when a strong base such as amide ion is used.

At present, the most useful tool in analyzing the ammonolysis products is infrared spectroscopy, and its function is entirely limited to the detection of Sb-NH-Sb and Sb=N=Sb linkages and possibly the Sb-NH bond for

triphenylstibine imine. The presence of iminobis-(triphenylchlorostibane) is readily detected by a band at 765 cm^{-1} which results from the Sb-NH-Sb stretching vibration. A band at 860 cm^{-1} is tentatively assigned to the Sb=N=Sb stretching vibration. This band is observed in all the ammonolysis products. An absorption occurring at 510 cm^{-1} appears to be associated with the 860 cm^{-1} band. It is probable that the higher energy band results from the asymmetrical stretching vibration and the lower energy band from the symmetrical stretching vibration. The Sb-NH stretching vibration from triphenylstibine imine is expected to occur close to 650 cm^{-1} since this is the region in which triphenylstibine oxide shows a strong absorption. The oxide and imine should be similar in structure and, therefore, give almost identical infrared spectra with the exception of the N-H stretching vibration. Ammonolysis products have been obtained on several occasions which show absorptions at 660 and 645 cm^{-1}. However, these bands always disappear during the purification process and as a result, no analytical results have been obtained for products containing these bonds.

Proton magnetic resonance data are so complicated that no useful conclusions may be drawn from them.

Pentaphenylstibane is probably produced from the reaction of tetraphenylbromostibane with potassium amide by

disproportionation of the original product, tetraphenylaminostibane. The reaction is postulated to proceed according to the following equation,

$$2(C_6H_5)_4SbNH_2 \rightarrow (C_6H_5)_5Sb + (C_6H_5)_3SbNH + NH_3 .$$

Triphenyldichlorostibane readily reacts with trimethylamine to form a 1:1 adduct. This reaction clearly shows that the dichlorostibane is capable of functioning as a Lewis acid and indicates that the first step in the ammonolysis reaction is probably the formation of a 1:1 adduct which readily splits out hydrogen chloride or potassium chloride. The infrared spectrum shows all the characteristic peaks of triphenyldichlorostibane and additional peaks at 3005, 2950, 2620, 2490, 1410, and 760 cm^{-1}. The first two peaks must result from C-H vibrations of the methyl groups of the amine and the 1410 cm^{-1} peak might be attributed to a C-H deformation mode. The 2620 and 2490 cm^{-1} bands are not assigned and the 760 cm^{-1} peak is assigned to the Sb-N stretching vibration.

CHAPTER IV

THE PREPARATION OF VARIOUS DERIVATIVES OF THE TYPE $(C_6H_5)_4SbX$

Experimental

Manipulation of materials

Tetraphenylbromostibane was purchased from Alfa Inorganics, Inc. and used as received. The material melted at 210-213°C. Solvents used for purification were of analytical reagent grade and were not dried.

Analytical methods

Elementary analyses were carried out by Schwarzkopf Microanalytical Laboratory, Woodside, New York.

Melting points were obtained using open capillaries on a Thomas-Hoover capillary melting point apparatus and are uncorrected.

Infrared spectra were obtained on a Beckmann Model IR 10 infrared spectrophotometer using cesium iodide optics. Solid state spectra were obtained using Nujol or Kel-F mulls. Infrared spectral absorptions are listed in Table 4.

Proton magnetic resonance spectra were obtained on a Varian nuclear magnetic resonance analytical spectrometer

TABLE 4

INFRARED SPECTRAL DATA, Cm^{-1} [a]

$(C_6H_5)_4SbOH$ Nujol	3605(w),3320(m,b),3050(m),1960(vvw,b), 1880(vvw,b),1815(vvw,b),1570(w), 1473(m),1430(s),1333(vw),1303(w), 1260(vw),1183(w),1158(vw),1075(w,sh), 1070(m,sh),1060(s),1020(m),998(m), 910(vvw),850(vvw),798(w,b),735(vs), 695(vs),660(w),648(w),613(vvw), 529(m),470(m,sh),455(s,sh),442(vs), 275(w,b),260(w)
$[(C_6H_5)_4Sb]_2O$ Nujol	3055(w),3030(w),3000(vw),1940(vvw,b), 1875(vvw,b),1800(vvw,b),1568(w), 1470(m),1428(s),1420(m),1325(vvw), 1298(vw),1252(vvw),1175(vvw,d), 1150(vvw),1068(w,sh),1061(m),1053(m), 1017(w),992(m),960(vvw),907(vvw), 845(vvw),735(vs),723(vs),690(vs), 650(s),640(m),460(s),452(m,sh), 442(m),330(w),280(w,b)
$(C_6H_5)_4SbONO_2$ Kel-F, Nujol	3040(w),1970(vvw,b),1882(vvw,b), 1815(vvw,b),1715(vvw,b),1650(vw,b), 1568(vw),1475(m),1428(vs),1330(vvw), 1290(vs,b),1170(vw),1155(vw), 1068(m),1018(m),815(vw),740(s,sh), 732(vs),688(vs),609(vvw),460(m,sh), 445(m),992(m)
$(C_6H_5)_4SbBr$ Nujol	3050(m,d),3000(w),1570(m),1470(s), 1430(s),1330(w),1300(w),1260(vw), 1195(vw,sh),1180(w),1156(w),1065(s), 1050(m),1019(w),992(s),910(vw), 840(vw),745(vs),730(vs),690(vs), 655(vw),610(vw),460(s),448(s), 280(w,b)

Table 4 (cont'd)

$[(C_6H_5)_4Sb]B(C_6H_5)_4$ Nujol	3140(vvw),3105(vvw),3040(m), 1875(vvw,b),1815(vw,b),1570(w), 1475(s),1432(s),1420(m),1330(w), 1302(vw),1260(vw,b),1170(w), 1130(vw),1062(m),1028(w),1018(vw), 992(m),975(vw),910(vvw),858(vvw,sh), 840(w),730(vs),702(vs),685(s), 620(vw),610(m),490(vvw),468(vvw), 452(w),439(w),275(vw,b)

[a]s, strong; m, medium; w, weak; sh, shoulder; b, broad; d, doublet; v, very.

Model A60-A. All spectra were obtained in deutero-chloroform using tetramethylsilane as an internal reference, except the spectrum of tetraphenylstibonium tetraphenylborate which was obtained in dimethyl sulfoxide. In some cases benzene was also used as an internal reference to facilitate the calculation of the chemical shift of the phenyl protons from the benzene signal.

Preparation of various compounds, $(C_6H_5)_4SbX$

The literature describes the preparation of a variety of compounds of the type $(C_6H_5)_4SbX$ (45,46,47), where X stands for Br, Cl, I, OH, ONO_2, $B(C_6H_5)_4^-$, etc. In all cases, the compounds were named as tetraphenylstibonium salts indicating that each was composed of the tetraphenylstibonium cation and the X anion. Since all data indicate that the Sb-X bonds in compounds of the type $(C_6H_5)_3SbX_2$ and R_3SbX_2 are partially covalent, it seems highly unlikely that these tetraphenyl compounds are truly ionic in nature. The only evidence put forward to verify the salt structure was the fact that they undergo various metathesis reactions and some are water soluble. We have prepared a few of these compounds in order to study their infrared and proton magnetic resonance spectra in hopes of finding some evidence for the partial covalency of the Sb-X bond. In most cases, no yield data were recorded.

Tetraphenylhydroxostibane

$$(C_6H_5)_4SbBr + OH^- \rightarrow (C_6H_5)_4SbOH + Br^-$$

An aqueous solution of tetraphenylbromostibane was treated with concentrated aqueous ammonia, immediately producing a white precipitate. The solid was filtered and washed until it was bromide free. No melting point is given as the material condenses with evolution of water at 110°C. (47).

Tetraphenylhydroxostibane is soluble in chloroform and relatively insoluble in water. Figure 59 shows the infrared spectrum. The infrared spectrum of tetraphenylbromostibane is shown in Figure 60 for comparison.

Anal. Calcd. for $(C_6H_5)_4SbOH$: C, 64.46; H, 4.73; Sb, 27.23. Found: C, 64.45; H, 4.80; Sb, 27.50.

Figure 61 shows the proton magnetic resonance spectrum of tetraphenylhydroxostibane. The peaks labelled A and A' are assigned to the ortho and to the meta and para protons of the phenyl groups, respectively. The area ratios between peaks A and A' could not be accurately measured because of the relative overlap of the signals. The peak labelled B, which occurs at 9.42 τ, is assigned to the proton attached to the oxygen atom. The area ratio between the phenyl peaks and the hydroxo peak is 20 to 0.74 as compared to an expected 20 to 1. The ortho proton pattern is shifted -23.7 cps from the benzene signal and the meta

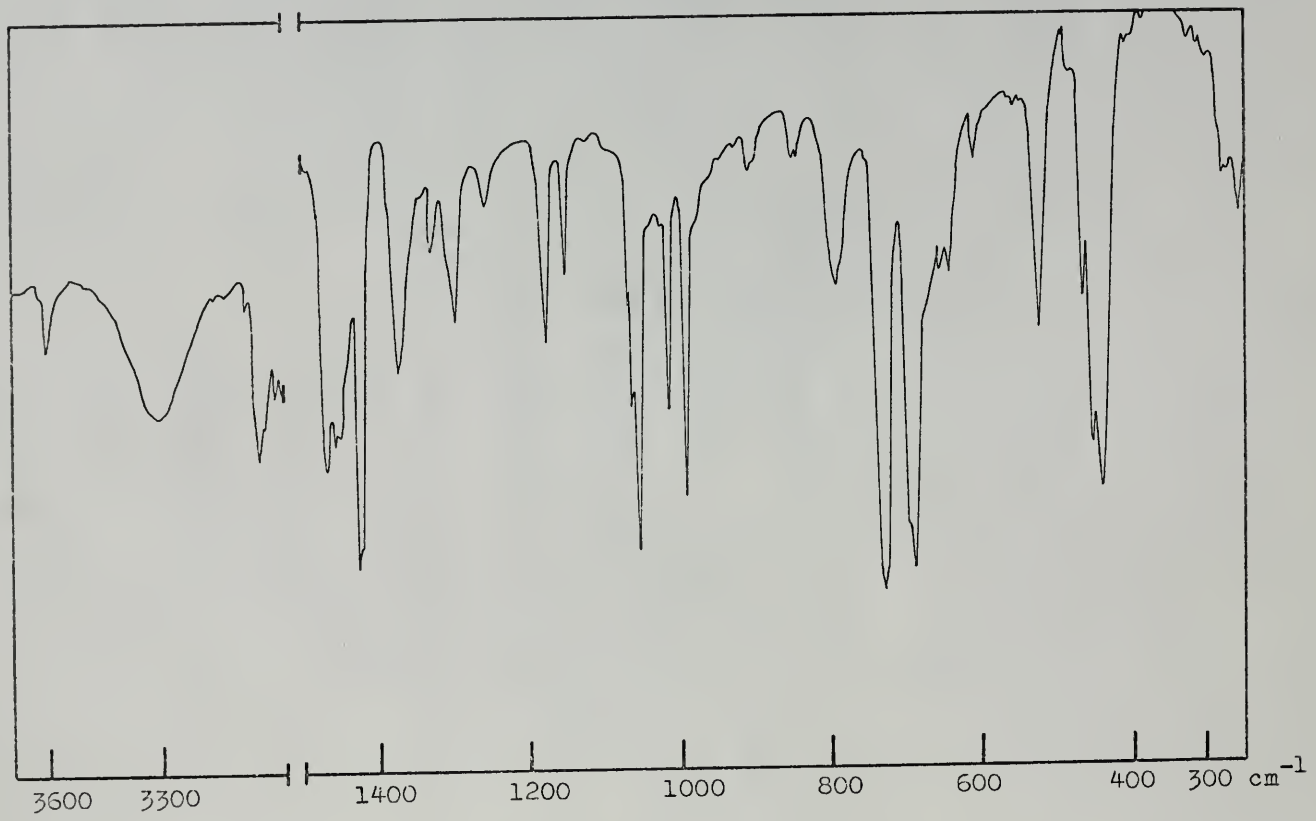


Fig. 59.-Infrared spectrum of $(C_6H_5)_4SbOH$.

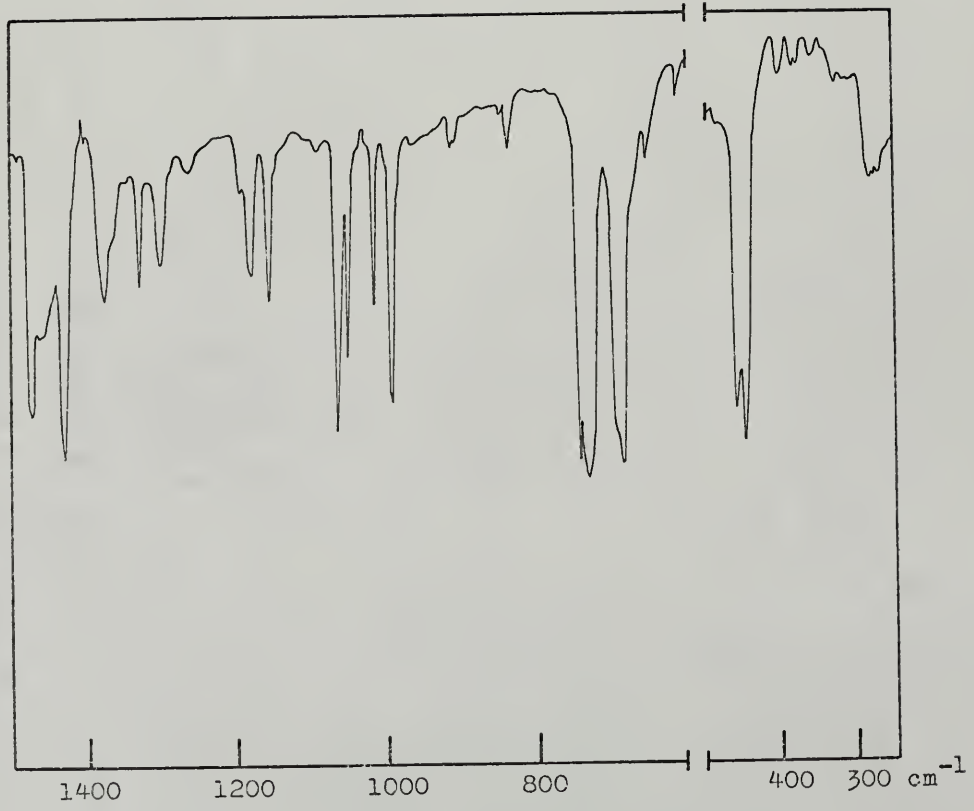


Fig. 60.-Infrared spectrum of $(C_6H_5)_4SbBr$.

Fig. 61.-Proton magnetic resonance spectrum of $(C_6H_5)_4SbOH$.

and para proton pattern is not significantly changed from benzene. For comparison, the proton magnetic resonance spectrum of tetraphenylbromostibane is shown in Figure 62.

Oxybis-(tetraphenylstibane)

$$2(C_6H_5)_4SbOH \xrightarrow{\Delta} [(C_6H_5)_4Sb]_2O + H_2O$$

A small sample of tetraphenylhydroxostibane was heated to 110°C. under full vacuum for several hours. The sealed reaction flask was transferred to a dry box to insure that the compound would not be exposed to moisture. Oxybis-(tetraphenylstibane) melted at 200-204°C.

The infrared spectrum of oxybis-(tetraphenylstibane) is shown in Figure 63. The peak at 656 cm^{-1} is assigned to the Sb-O-Sb asymmetrical stretching vibration and is indicative of a covalent antimony-oxygen bond. The medium peak at 330 cm^{-1} might result from the symmetrical Sb-O-Sb vibration.

Anal. Calcd. for $[(C_6H_5)_4Sb]_2O$: C, 65.78; H, 4.60; Sb, 27.79. Found: C, 65.59; H, 4.76; Sb, 27.67.

Proton magnetic resonance data were not obtained.

Tetraphenylnitratostibane

$$(C_6H_5)_4SbBr + NO_3^- + Ag^+ \rightarrow (C_6H_5)_4SbONO_{2(aq)} + AgBr$$

A water solution of tetraphenylbromostibane was treated with aqueous silver nitrate. The solution was filtered free of silver bromide and then was evaporated by

Fig. 62.--Proton magnetic resonance spectrum of $(C_6H_5)_4SbBr$.

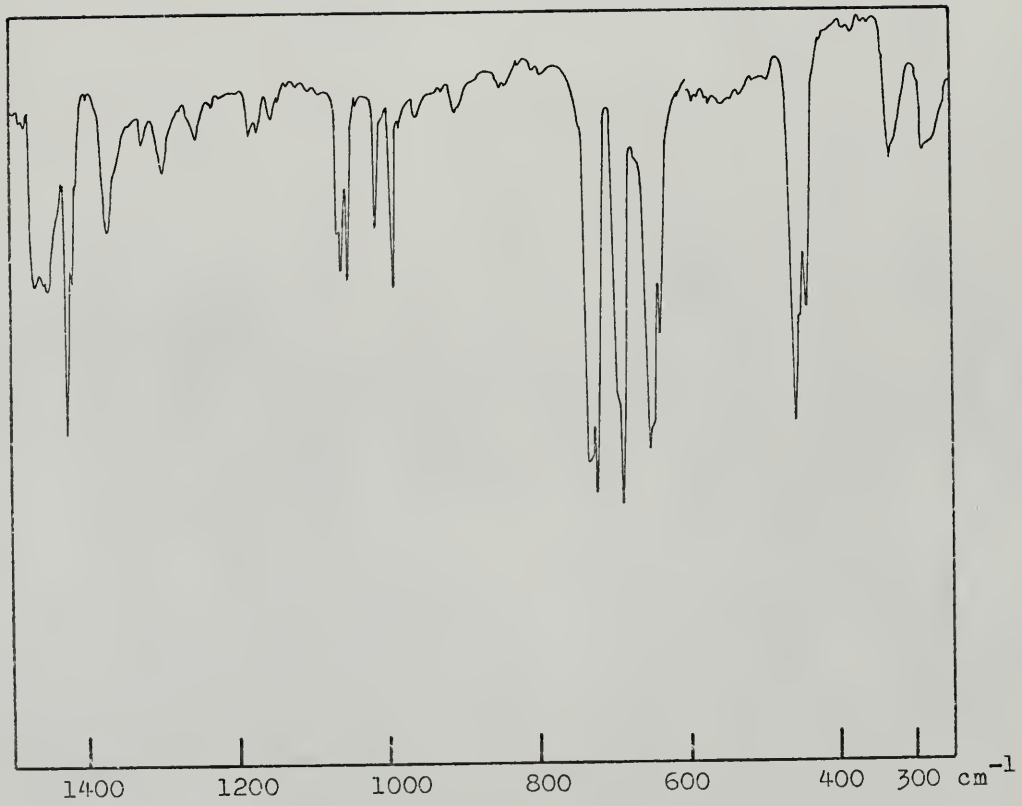


Fig. 63.-Infrared spectrum of $[(C_6H_5)_4Sb]_2O$.

vacuum until a white solid crystallized. The solid was dried by vacuum and melted at 182-183°C.

Tetraphenylnitratostibane is soluble in large quantities of water, but can be recrystallized from small quantities. The compound is also soluble in chloroform. The infrared spectrum is shown in Figure 64. The covalent nitrato peaks, ν_4 and ν_1, are observed at 1430 cm^{-1} and 1291 cm^{-1}, respectively. The $\nu_4 - \nu_1$ splitting is 139 cm^{-1} which indicates that the antimony-nitrato linkage is somewhat covalent in nature. The characteristic ν_2 mode is not seen, but is suspected of being overlapped by the phenyl absorption at 1018 cm^{-1}. This phenyl peak is normally very sharp and of considerable less intensity than the phenyl peak at 992 cm^{-1}, however, in this compound the 1018 cm^{-1} band is not sharp and is of almost equal intensity as the 992 cm^{-1} band. The ν_3, ν_5 and ν_6 modes are either not present or are overlapped by other absorptions.

Anal. Calcd. for $(C_6H_5)_4SbONO_2$: C, 58.57; H, 4.10; N, 2.85; Sb, 24.74. Found: C, 58.34; H, 4.14; N, 2.87; Sb, 24.95.

Figure 65 shows the proton magnetic resonance spectrum of tetraphenylnitratostibane. The rather complex peak is assigned to the phenyl protons; however, in this case the chemical shift value for the ortho protons is not significantly different from that of the meta and para

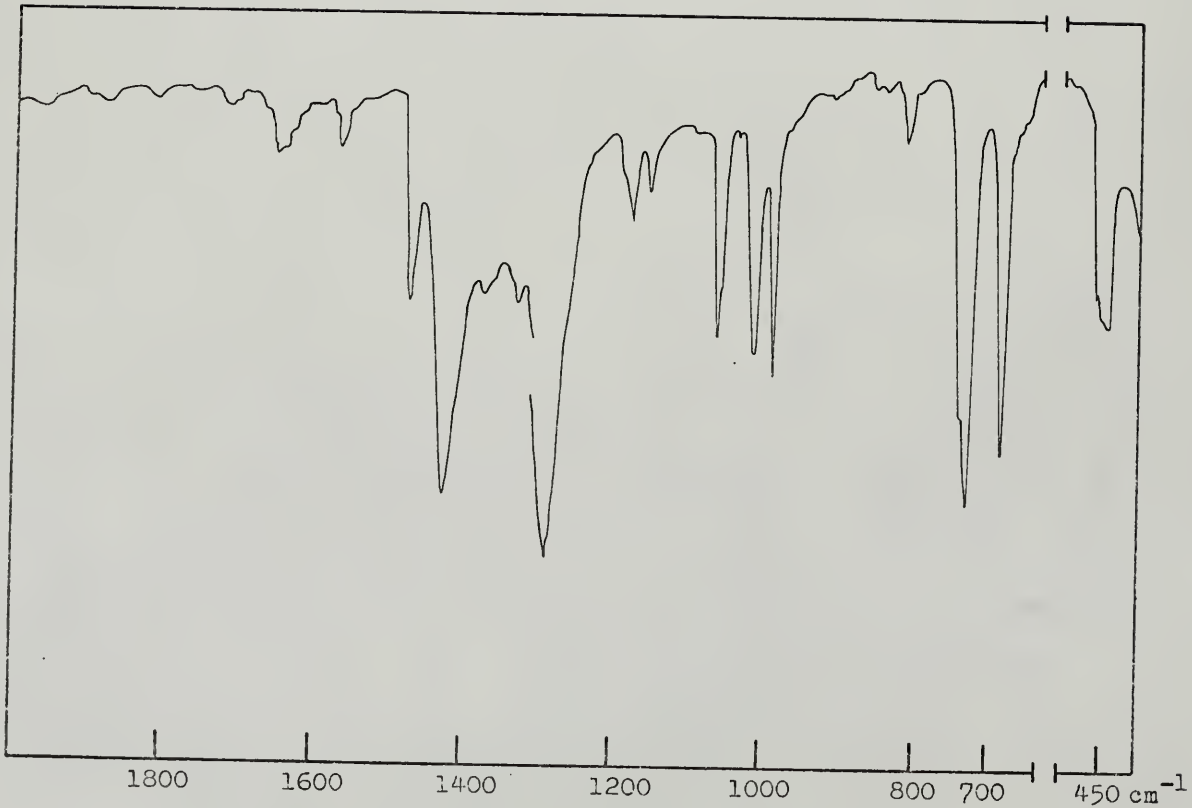


Fig. 64.-Infrared spectrum of $(C_6H_5)_4SbONO_2$.

Fig. 65.-Proton magnetic resonance spectrum of $(C_6H_5)_4SbONO_2$.

protons and therefore no splitting occurs. The chemical shift from benzene was not measured.

Tetraphenylstibonium tetraphenylborate

$$(C_6H_5)_4SbBr_{(aq)} + (C_6H_5)_4BNa_{(aq)} \rightarrow [(C_6H_5)_4Sb]B(C_6H_5)_4$$

Tetraphenylstibonium tetraphenylborate was prepared by mixing aqueous solutions of tetraphenylbromostibane and sodium tetraphenylborate. An immediate white precipitate resulted which was recrystallized from nitromethane and found to melt at 253-258°C. (dec.) [Lit. (48) m.p. 258-260°C. (dec.)]. No yield data were recorded as this compound was prepared for an infrared and proton magnetic resonance study.

The infrared spectrum of tetraphenylstibonium tetraphenylborate is shown in Figure 66. Peaks seen in both starting materials are observed in the spectrum of the salt with only minor shifts in some cases. A new peak resulting from tetracoordinate antimony attached to one or more phenyl groups is not seen as it is in the case of tetracoordinate phosphorus attached to one or more phenyl groups.

Elemental analyses were not obtained.

The proton magnetic resonance spectrum of tetraphenylstibonium tetraphenylborate is shown in Figure 67. The spectrum was taken as a saturated solution in dimethyl sulfoxide with about 10 per cent by volume of benzene added. The peak labelled A is assigned to the phenyl protons of the

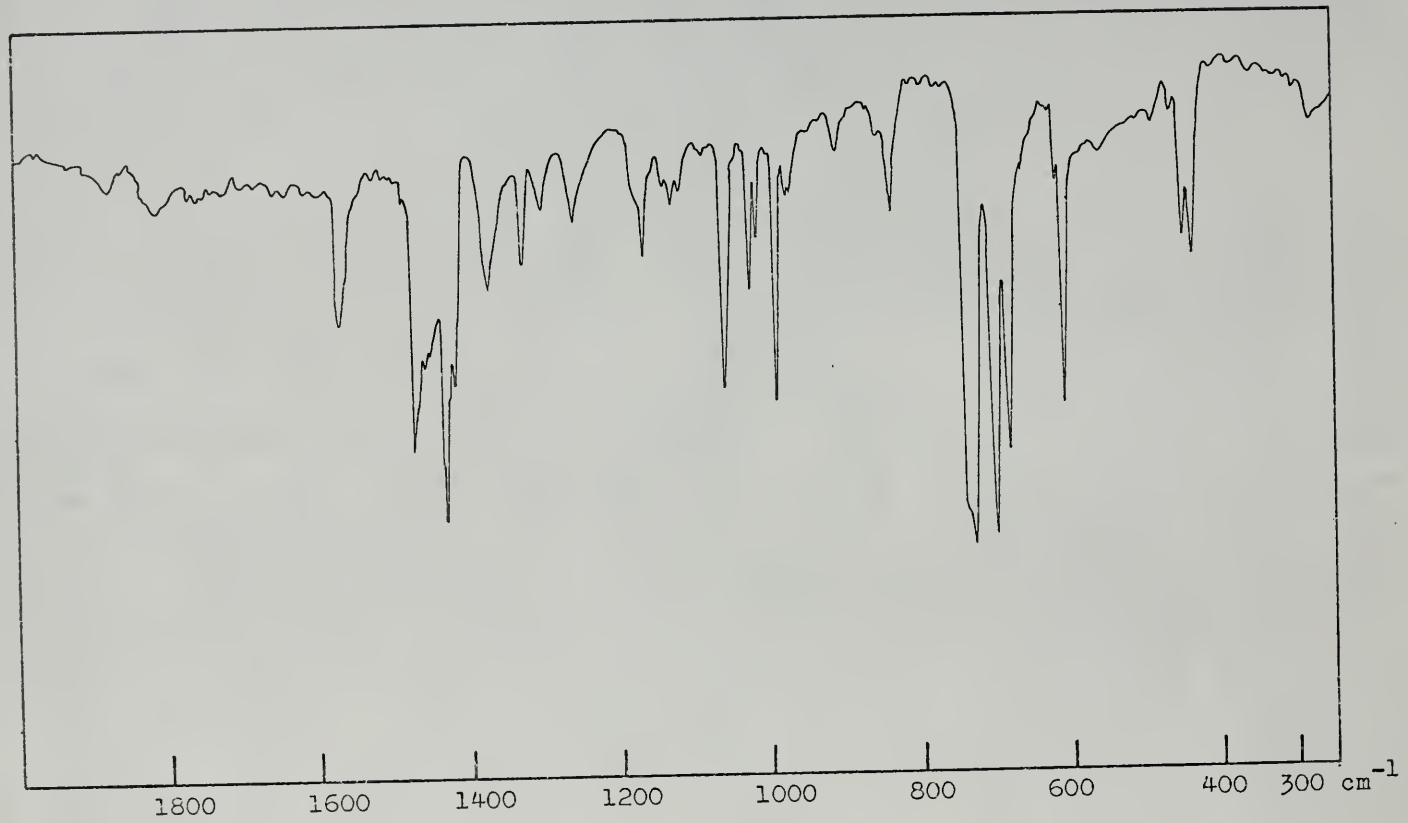


Fig. 66.-Infrared spectrum of $[(C_6H_5)_4Sb]B(C_6H_5)_4$.

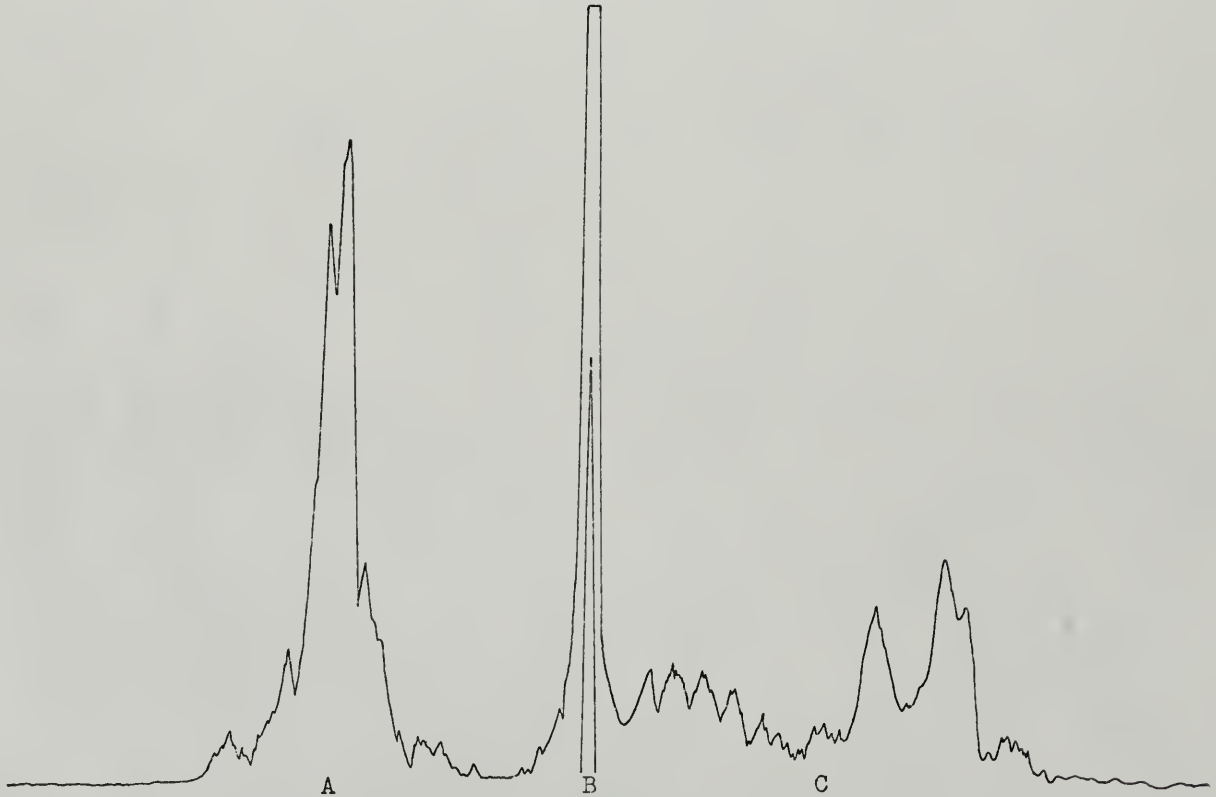


Fig. 67.-Proton magnetic resonance spectrum of $[(C_6H_5)_4Sb]B(C_6H_5)_4$.

tetraphenylstibonium ion and the peak labelled C to the tetraphenylborate ion. Peak B results from benzene which was used as an internal reference. This spectrum illustrates the fact that an electron withdrawing group, Sb^+, causes a downfield shift from the benzene signal and an electron donating group, B^-, causes an upfield shift from benzene.

Discussion

To prove the actual existence of the tetraphenylstibonium cation in compounds of the type $(C_6H_5)_4SbX$, where X is Br, OH, or ONO_2, would require a much more extensive study than the present one and would eventually include a complete single crystal x-ray analysis of the respective compounds. The present study involves a qualitative infrared analysis of five derivatives of which only $[(C_6H_5)_4Sb]B(C_6H_5)_4$ certainly contains the tetraphenylstibonium cation. The infrared spectra of the five compounds are presented for the first time and the melting point of tetraphenylnitratostibane is also reported. Proton magnetic resonance data are presented for all of the compounds.

The solid state infrared spectrum of tetraphenylhydroxostibane shows all the characteristic peaks associated

with the phenyl groups plus other bands at 3605 (weak), 3310 (medium and broad), 795 (medium) and 528 (medium to strong) cm^{-1}. The 3605 cm^{-1} band results from the free O-H stretching vibration and the 3310 cm^{-1} band results from the intermolecular hydrogen bonded O-H stretching vibration. The hydrogen bonding is probably of a polymeric nature. The intensity of the 3605 cm^{-1} band is greatly increased with respect to the 3310 cm^{-1} band when the spectrum is recorded as a dilute chloroform solution. This shows that the amount of hydrogen bonding is reduced in solution thereby giving rise to a stronger free O-H stretching vibration.

Attempts to prepare $(C_6H_5)_4SbOD$ produced a mixture of the -OH and -OD derivatives. Examination of the infrared spectrum of this mixture taken as a dilute solution in carbon tetrachloride revealed the presence of the free O-H absorption at 3320 cm^{-1} and the free O-D absorption at 2680 cm^{-1}. The bands at 795 and 528 cm^{-1} were unaffected by partial deuteration and no new bands were seen. Therefore, it seems likely that the latter two bands are associated with vibrations resulting from the Sb-OH group rather than with low energy deformation modes of the O-H group.

When tetraphenylhydroxostibane is heated to 110°C. under vacuum, condensation occurs with loss of water. The

resulting compound is oxybis-(tetraphenylstibane). The infrared spectrum of this anhydride does not show any of the four bands mentioned above which are associated with the O-H and Sb-OH stretching vibrations, but does show a strong absorption at 655 cm^{-1} and a weak band at 330 cm^{-1}. The 655 cm^{-1} band is attributed to the Sb-O-Sb asymmetrical stretching vibration, whereas no assignment is made for the 330 cm^{-1} band although it might well result from the Sb-O-Sb symmetrical stretching vibration. It should be pointed out that triphenylstibine oxide, which is thought to be polymeric with long chains of Sb-O linkages, also shows a strong absorption in this same region. The mere presence of this absorption is indicative of a partially covalent Sb-O bond. There, of course, would be no absorption if the molecule were salt-like containing tetraphenylstibonium cations and oxide anions.

The infrared spectrum of tetraphenylbromostibane shows only absorptions which can be attributed to the normal vibrations of the phenyl group. The Sb-Br stretching vibration probably occurs in the 240 cm^{-1} region.

The infrared spectrum of tetraphenylnitratostibane shows all bands associated with the phenyl groups plus bands which result from the covalent nitrato group. The ν_4 and ν_1 peaks occur at 1430 and 1291 cm^{-1}, respectively, and represent a splitting of 139 cm^{-1}. This splitting is greater

than the 125 cm^{-1} splitting used as the upper limit criterium for splitting caused by lattice distortion and is therefore assumed to result from coordination between the antimony and an oxygen atom of the nitrato group. As mentioned earlier, the characteristic ν_2 mode of the covalent nitrato group is not seen, but is suspected of being masked by the phenyl band at 1018 cm^{-1}. The other absorptions, ν_3, ν_5, and ν_6, do not appear to be present, but also might be overlapped by phenyl absorptions in the 700 cm^{-1} region.

The infrared spectrum of the only true stibonium salt included in this study, tetraphenylstibonium tetraphenylborate, shows bands which can only be associated with vibrations characteristic of phenyl groups. Bands seen in both starting materials are present with only minor shifts in frequency in some cases. No peak is present which might be attributed to tetracoordinate antimony attached to one or more phenyl groups as is the case with corresponding phosphorus compounds.

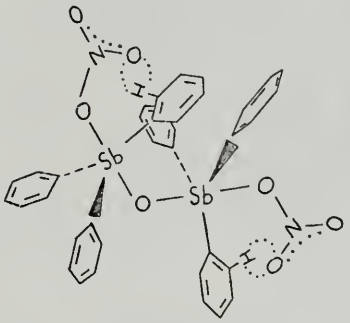
The proton magnetic resonance spectrum of tetraphenylhydroxostibane shows the phenyl signal as two distinct sets of peaks. Accurate area ratios could not be determined, but on the basis of the information gained from the triphenylantimony derivatives, the signal furthest downfield is assigned to the ortho protons of the phenyl groups and

the upfield signal to the meta and para protons. The ortho proton signal is shifted -23.7 cps from the benzene signal while the meta and para proton signal is not significantly moved from the benzene signal. This suggests that the Sb-OH group is electron withdrawing thereby causing the ortho proton signal to be shifted downfield from the meta and para proton signal. This is quite reasonable since the ortho protons, which are adjacent to the electron withdrawing group, should experience greater deshielding than the other protons on the phenyl group.

The proton magnetic resonance spectrum of tetraphenylnitratostibane shows only one complex peak for the phenyl groups. The chemical shift values for the ortho, meta and para proton signals are not sufficiently different and as a result only one complex peak is seen. Since the spectrum was not recorded in the presence of benzene, the exact position of the phenyl signal with respect to this reference is not known.

In the nitrato compounds considered in this study, oxybis-(triphenylnitratostibane) and tetraphenylnitratostibane, the chemical shift values for the ortho, meta, and para proton signals have been similar, whereas the ortho proton signal in the chloro and bromo derivatives has been shifted downfield from both the benzene signal and the meta and para proton signal. A downfield shift from benzene, or

as the case may be, a downfield shift from the meta and para signal indicates that the ortho protons are screened less efficiently than the others. In all cases involving phenyl groups directly attached to antimony, only the ortho protons appear to be significantly effected by the electron withdrawing character of antimony and it is therefore assumed that the phenyl signal of the nitrato compounds must be in the near vicinity of the benzene signal. In other words, the ortho protons in the nitrato compounds must undergo screening from another source, and it must nullify the deshielding effect of the antimony atom. The two free oxygen atoms of the nitrato group might produce such an effect in a manner shown below.



Proton magnetic resonance data for the tetraphenyl derivatives indicate the presence of equivalent phenyl groups which is suggestive of the square pyramidal structure with the phenyl groups at the base and the X substituent at the apex. The structures of the tetraphenyl derivatives have

not been determined. Since the proton magnetic resonance spectrum of tetraphenylnitratostibane is similar to that for the compound shown above, it is concluded that the same type of interaction between an oxygen atom of the nitrato group and the ortho protons of the phenyl groups must take place.

The proton magnetic resonance spectrum of tetraphenylstibonium tetraphenylborate was obtained in dimethyl sulfoxide using benzene as an internal reference. This spectral pattern readily demonstrates the effect that electron withdrawing and electron donating groups have on the proton signals of a phenyl group. The signal for the tetraphenylstibonium cation (electron withdrawing) is shifted -22 cps from the benzene signal, whereas the signal for the tetraphenylborate anion (electron donating) is shifted approximately +16 cps from the benzene signal. The relative shifts cannot be compared to those of the other compounds since a different solvent was used.

CHAPTER V

GENERAL CONCLUSIONS

This work has definitely established the generality of the chloramine-tertiary stibine reaction and has shown that the reaction is analogous to that between chloramine and tertiary amines, phosphines, and arsines. Preliminary results obtained from ammonolysis reactions suggest that polymeric compounds might be obtained from reactions of this type. The antimony-nitrogen compounds produced in these studies are moisture sensitive to varying degrees and must be handled in extremely dry atmospheres. No structure determinations were performed, but infrared analyses indicate that antimony is pentavalent in all compounds included in this study except tetraphenylstibonium tetraphenylborate. Infrared data are summarized in each chapter and proton magnetic resonance data are compiled in Table 7.

Trialkylstibines (CH_3-, C_2H_5-, n-C_3H_7- and n-C_4H_9-) and triphenylstibine react with chloramine to produce the corresponding iminobis-(trialkylchlorostibanes) and iminobis-(triphenylchlorostibane) in good yields. The reaction is postulated to proceed according to the following equations:

$$R_3Sb + NH_2Cl \rightarrow R_3Sb(NH_2)Cl$$

$$2R_3Sb(NH_2)Cl \rightarrow [R_3Sb(Cl)]_2NH + NH_3$$

Since all available data from the literature indicate that compounds of the type R_3SbCl_2 are not stibonium salts, it is reasonable to assume that $R_3Sb(NH_2)Cl$ is also not a stibonium salt. If this assumption is true, little or no stability would be gained from ionic lattice energy and condensation would be expected to readily occur to produce the more stable imino compound.

The low-temperature reaction of chloramine with trimethylstibine does not yield aminotrimethylchlorostibane as expected, but instead, yields a thermally unstable species with an Sb:N:Cl ratio identical with that in iminobis-(trimethylchlorostibane). This low-temperature species must in some way be involved in the side reaction that occurs in the case of trimethylstibine in which trimethyldichlorostibane is produced in variable yields. This type of reaction also occurs in the case of triphenylstibine. The reaction is postulated to proceed according to one of the following equations:

$$R_3Sb(NH_2)Cl + NH_2Cl \rightarrow R_3SbCl_2 + 1/3N_2 + 4/3NH_3$$

or

$$2R_3Sb(NH_2)Cl \rightarrow R_3SbCl_2 + R_3Sb + 1/3N_2 + 4/3NH_3$$

However, it is quite probable that other thermally unstable intermediate compounds are involved. The factors that control the chlorination reaction are not known, but preliminary experiments indicate that the reaction is more dependent upon concentration than upon mole ratios of starting materials. Furthermore, there is a strong similarity between this chlorination reaction and that which occurs between tri-n-butylstibine and antimony(III) chloride.

The low-temperature ammonolysis of triphenyldichlorostibane leads to antimony-nitrogen compounds that are best described by the following formula:

$$\left\{(C_6H_5)_3Sb{=}N{-}\left[{-}Sb(C_6H_5)_3{-}N{=}\right]_{1-x}Sb(C_6H_5)_3\right\}xCl\cdot zKCl$$

The exact nature of the product has not been established, but it is almost certain to be a mixture of precursors to triphenylstibine imine. The significance of the ammonolysis reaction lies in the fact that the reaction will probably provide a direct route to antimony-nitrogen polymers. To be more specific, the ammonolysis of compounds of the type R_2SbX_3 and $RSbX_4$ should result in the formation of polymers such as $-\left[R_2SbN\right]_x-$ and highly cross-linked polymers.

It has been shown that the chloramination and ammonolysis products readily react with water to produce ammonia and antimony-oxygen compounds. Since the normal method used for the production of chloramine does not

rigorously exclude moisture, a new procedure had to be developed that required the use of ammonia-free chloramine and vacuum line technique. Ammonia-free chloramine is not essential, but the anhydrous copper sulfate used for removing ammonia also removes water quite effectively. The ethereal ammonia-free chloramine is then transferred into a vacuum line without exposure to moisture and distilled away from any solid impurities.

The hydrolysis of the chloramination products is postulated to proceed according to the following equation:

$$[R_3Sb(Cl)]_2NH + H_2O \rightarrow [R_3Sb(Cl)]_2O + NH_3$$

The anhydrides obtained from the above reaction are more stable than the imino compounds with respect to thermal decomposition and as a result are much more easily recrystallized from common organic solvents.

The chlorine atoms were replaced with nitrato groups in a variety of the anhydrides and the resulting compounds were studied by infrared spectroscopy. The results clearly show that the Sb-O-NO_2 linkage is partially covalent. Table 5 lists the absorptions which result from the nitrato group. This conclusion is postulated to also hold for the Sb-Cl linkage in the anhydride and imino compounds. This cannot be proven since the Sb-Cl absorption is either overlapped by other absorptions in the 300-250 cm^{-1} region, too weak to be resolved from the background, or out of range of the

TABLE 5

NITRATO ABSORPTION FREQUENCIES IN $[R_3Sb(ONO_2)]_2O$ COMPOUNDS (Cm^{-1})[a]

C_{2v}	$[(CH_3)_3Sb(ONO_2)]_2O$	$[(C_2H_5)_3Sb(ONO_2)]_2O$	$[(C_6H_5)_3Sb(ONO_2)]_2O$
$\nu_2 + \nu_4$	2440 vw,d		
$\nu_1 + \nu_2$	2290 vw	2285 vw	
$2\nu_2$	2010 vw,d		
$\nu_2 + \nu_3$ or ν_5	1720 w	1715 vw	
ν_4	1480-1380 vs,b[b]	1480-1420 vs[b]	1505 m,sh; 1495 s
ν_1	1310-1275 vs,b	1285 vs	1275 s
ν_2	1018 vs	1025 s,sh	975 s
ν_6	815 vs,sh	815 s,sh	805 m
ν_3 or ν_5	715 vs	----------[c]	708 vs

[a]vs, very strong; s, strong; m, medium; w, weak; vw, very weak; sh, shoulder; b, broad; d, doublet.

[b]Overlaps C-H def. modes.

[c]Covered by CH_2 rock.

instrument. Far infrared and Raman experiments would probably provide valuable data.

A variety of compounds of the type $(C_6H_5)_4SbX$, where X is -OH, $-ONO_2$, -Br, and $B(C_6H_5)_4^-$, and $[(C_6H_5)_4Sb]_2O$ were also studied by infrared spectroscopy. The results indicate that the Sb-X bond and the Sb-O-Sb linkage are at least partially covalent in character. The only true stibonium salt included in the study, tetraphenylstibonium tetraphenylborate, does not show any bands which might be associated with tetracoordinate antimony, or which would be analogous to the 8.9 μ band for phenylphosphonium salts.

Infrared data for individual compounds are tabulated at the beginning of each chapter and discussed at the end of the given chapter. The spectra of the imino compounds show the characteristic $\geq$N-H stretching vibration in the 3225-3140 cm^{-1} region and fail to show any $\geq$N-H deformation mode, and the spectra of the anhydrides fail to show any absorption which can be assigned to the O-H vibration. These data are in complete agreement with the proposed structures. All the imino and anhydride compounds show a strong absorption in the 792-734 cm^{-1} region. This region is assigned to the Sb-NH-Sb and Sb-O-Sb vibration. Frequencies for the Sb-NH-Sb and Sb-O-Sb absorptions for a variety of compounds are compiled in Table 6. The Sb-O vibration occurs in the 655 cm^{-1} region for triphenylstibine

TABLE 6

Sb–O–Sb AND Sb–NH–Sb INFRARED FREQUENCIES (Cm^{-1})

Compound	Frequency
$[(CH_3)_3Sb(Cl)]_2NH$	741
$[(CH_3)_3Sb(Cl)]_2O$	775[13]
$[(CH_3)_3Sb(ONO_2)]_2O$	788
$[(CH_3)_3Sb(ClO_4)]_2O$	775[13]
$[(C_6H_5CH_2)_3Sb(Cl)]_2O$	766[a]
$[(C_2H_5)_3Sb(Cl)]_2NH$	751
$[(C_2H_5)_3Sb(Cl)]_2O$	768
$[(C_2H_5)_3Sb(ONO_2)]_2O$	792
$[(\underline{n}\text{-}C_3H_7)_3Sb(Cl)]_2NH$	752
$[(\underline{n}\text{-}C_3H_7)_3Sb(Cl)]_2O$	754 or 734
$[(\underline{n}\text{-}C_4H_9)_3Sb(Cl)]_2NH$	768 or 736
$[(\underline{n}\text{-}C_4H_9)_3Sb(Cl)]_2O$	743
$[(C_6H_5)_3Sb(Cl)]_2NH$	768
$[(C_6H_5)_3Sb(Cl)]_2O$	768 (762,769[14])
$[(C_6H_5)_3Sb(ONO_2)]_2O$	740[b] (736, br[14])
$[(C_6H_5)_3Sb(Br)]_2O$	772, 764[14]
$[(C_6H_5)_3Sb(ClO_4)]_2O$	751, 738[14]
$[(C_6H_5)_3Sb\text{–}O\text{–}Sb(C_6H_5)_3]SO_4$	740, br[14]
$[(C_6H_5)_2Sb(Cl)_2]_2O$	783[a]

[a] Private communication with L. Kolditz (12).

[b] Overlapped by phenyl absorption in 740 cm^{-1} region.

oxide and the partially hydrated species. The Sb-O-Sb vibration for $[(C_6H_5)_4Sb]_2O$ also occurs in the 655 cm^{-1} region.

All the alkyl imino and anhydride compounds exhibit an Sb-C asymmetrical stretching vibration in the 591-500 cm^{-1} region and the phenyl analogues exhibit this vibration around the 450 cm^{-1} region. Also, an absorption was found at 534 cm^{-1} and below for $[R_3Sb(X)]_2NH$ and $[R_3Sb(X)]_2O$, where R is methyl or ethyl and X is a chloro or nitrato group, which may result from the Sb-C symmetrical stretching vibration. The bands at 860 and 510 cm^{-1} are tentatively assigned to the Sb=N=Sb vibration.

Proton magnetic resonance data are compiled in Table 7. In most cases the data are entirely consistent with that to be expected for the particular compound in question. In other words, the spectra of the imino and anhydride species show only one kind of alkyl or phenyl group. The spectra for the tetraphenyl species show only equivalent phenyl groups as does the spectrum of pentaphenylstibane.

Figure 68 shows the results of a study in which the proton absorptions from the phenyl group attached to antimony are compared to the proton signal from benzene (32). A downfield shift from the benzene signal is designated as a negative shift and an upfield shift is designated as a positive shift. A negative shift from the benzene signal

TABLE 7

PROTON MAGNETIC RESONANCE DATA, τ[a]

Compound	CH_3	CH_2	C_6H_5	Solvent[b]
$[(CH_3)_3Sb(Cl)]_2NH$	7.57,7.82,7.97			
$[(CH_3)_3Sb(Cl)]_2O$	7.92			H_2O
	7.65,7.97,8.05			
$[(CH_3)_3Sb(ONO_2)]_2O$	7.95			H_2O
	8.03,8.10,8.45			
$[(C_2H_5)_3Sb(Cl)]_2NH$[c]	8.45	7.63		
$[(C_2H_5)_3Sb(Cl)]_2O$	8.39	7.37		H_2O
	8.55[c]	7.85		C_6H_6
$[(\underline{n}\text{-}C_3H_7)_3Sb(Cl)]_2NH$	8.97	7.[illegible]-8.53 (range)		
$[(\underline{n}\text{-}C_3H_7)_3Sb(Cl)]_2O$	8.97	7.43-8.55 (range)		CCl_4
$(\underline{n}\text{-}C_4H_9)_3Sb$	9.10	8.18-8.87 (range)		Pure
$[(\underline{n}\text{-}C_4H_9)_3Sb(Cl)]_2NH$	8.88	7.05-8.9 (range)		
$[(C_6H_5)_3Sb(Cl)]_2NH$			1.96-2.80 (range)	
$[(C_6H_5)_3Sb(Cl)]_2O$			2.08-2.80 (range)	
$[(C_6H_5)_3Sb(ONO_2)]_2O$			2.06-2.74 (range)	

Table 7 (cont'd)

Compound	CH_3	CH_2	C_6H_5	Solvent[b]
$(CH_3)_3Sb(ONO_2)_2$	7.83			
$(CH_3)_3SbCl_2$	7.56			
$(CH_3)_3SbBr_2$	7.28			
$(C_6H_5)_3Sb$			2.44-2.96 (range)	
$(C_6H_5)_3SbCl_2$			1.54-1.90, 2.24-2.62 (range)	
$(C_6H_5)_3SbO \cdot 0\ 3H_2O$			1.85-2.28, 2.28-2.76 (range)	
$(C_6H_5)_5Sb$[d]			2.42-3.04 (range)	
$[(C_6H_5)_3Sb{=}N{=}Sb(C_6H_5)_3]Cl_2K$ 0.8 C_7H_8			1.90-2.22, 2.22-2.79 (range)	
$(C_6H_5)_3SbCl_2 \cdot N(CH_3)_3$	7.53		1.38-1.78, 2.02-2.76 (range)	
$(C_6H_5)_4SbOH$[d]			2.10-2.48, 2.48-2.90 (range)	
$(C_6H_5)_4SbBr$[d]			2.01-2.40, 2.40-2.80 (range)	
$(C_6H_5)_4SbONO_2$[d]			2.13-2.75 (range)	

[a] External standards were used unless otherwise indicated.
[b] $CDCl_3$ was used as a solvent unless otherwise indicated.
[c] Internal standard was used (C_6H_6).
[d] Internal standard was used [$(CH_3)_4Si$].

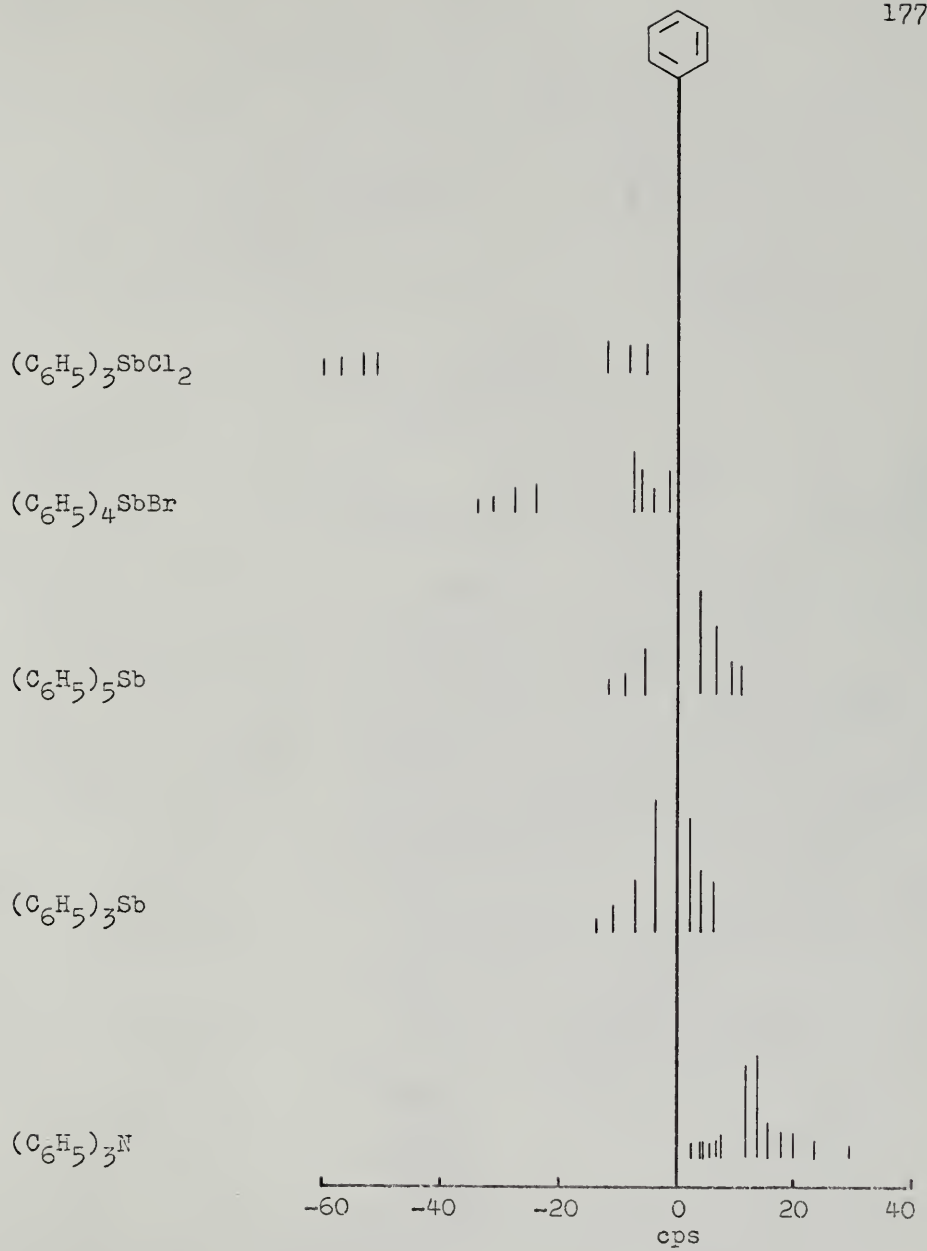


Fig. 68.--Comparison of phenyl proton signals from various antimony compounds with that from benzene.

is asscciated with proton descreening and is indicative of an electron withdrawing group attached to the phenyl ring, whereas a positive shift is associated with proton screening and is indicative of an electron donating group attached to the phenyl ring. This experiment readily shows that an antimony atom functions as an electron withdrawing group when it is also bonded to one or more electronegative atoms, such as oxygen, chlorine or bromine. Since the para proton signal does not appear to be shifted with respect to the benzene signal in the compounds included in this study, it is probable that the descreening of the ortho protons arises from a magnetic anisotropic effect rather than a resonance effect, which would certainly extend to the para position.

The fact that there is no apparent shift of the ortho proton signal from that of the meta and para proton signal when a nitrato group is bonded to antimony is not understood.

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BIOGRAPHICAL SKETCH

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This dissertation was prepared under the direction of the chairman of the candidate's supervisory committee and has been approved by all members of that committee. It was submitted to the Dean of the College of Arts and Sciences and to the Graduate Council, and was approved as partial fulfillment of the requirements for the degree of Doctor of Philosophy.

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